Vol. VI. [MARCH, 1884.] No. 1.

AMERICAN CHEMICAL JOURNAL.

ON THE REVERSION OF PHOSPHORIC ACID.

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In a previous paper[1] the writer has demonstrated, among minor considerations, the following points:

I. That reverted phosphoric acid exists in three forms in commercial superphosphates:

(*a*) as reverted phosphate of lime,
(*b*) " " " " iron,
(*c*) " " " " alumina.

II. That artificially precipitated phosphate of lime, whether the di-calcic or tri-calcic form, when mixed with sulphate of lime (as is the case in a superphosphate) and exposed to atmospheric conditions in shade in open vessels for several days and dried to a fine powder, is readily and completely soluble in a neutral solution of citrate of ammonia, at the temperature of 40° C.

III. That artificially precipitated phosphates of iron and alumina, when treated in the same way, become largely insoluble in the citrate of ammonia solution, at the temperature of 40° C.

IV. That a citrate of ammonia solution alone, of all the solvents that have been proposed, is a perfect solvent for all the forms of reverted phosphates (as they exist in superphosphates), while at the same time it does not unduly dissolve the crude or insoluble phosphate present.

[1] This Journal, **4**, 123; and Chemical News, **46**, 18, 31.

V. Lastly, and most important of all, the citrate of ammonia solution, in order to be a perfect solvent for reverted phosphates of iron and alumina, as they exist in commercial superphosphates, must be used at a temperature of 65° C. (150° F). At this temperature every form of reverted phosphate is dissolved.

In the present publication the above points are more fully sustained by additional experiments, and the investigation has been extended to a consideration of the reversion of soluble phosphates in artificial and natural soils.

The inquiry may be divided for the sake of clearness into the following heads:

I. Experiments on natural phosphates,
II. " " artificial soils,
III. " " natural "

I.—Experiments on Natural Phosphates.[1]

To make the investigation on this point as conclusive as possible, a very large number of natural phosphates, embracing nearly every commercial article, was collected. These samples were all ground to pass through a 60 mesh sieve; no further grinding nor trituration being employed. Several liters of a neutral citrate of ammonia solution, specific gravity 1.09, were prepared. One gram of each phosphate was accurately weighed, and washed into a 200 cc. flask with 50 cc. of the above solution. The flask was corked and the contents digested for 30 minutes as follows:

1st. One gram with neutral solution at temp. of 40° C.
2d. " " " " " " " 65° C.
3d. " " " ammoniacal " " " " "
4th. " " " stronger " " " " " "
5th. " " " acid " " " " "

In digestion 3d, ½ cc. of 20 per cent. ammonia solution was added to every 50 cc. solution of citrate of ammonia.

In digestion 4th, 1 cc. of 20 per cent. ammonia solution was added to every 50 cc. of citrate of ammonia solution.

In digestion 5th, .753 gram of citric acid was added to every 50 cc. of citrate of ammonia solution. This quantity is just equivalent to .200 gram of ammonia, the amount of free ammonia added to every 50 cc. in digestion 4th.

[1] For many of the samples used thanks are due to Dr. C. U. Shepard, Jr.

Lime Phosphates.

No.	Commercial Name.	Digestion 1st. With neutral citrate of ammonia solution, temperature 40° C. Per cent. Phos. acid dis.	Digestion 2d. With neutral citrate of ammonia solution, temperature 65° C. Per cent. Phos. acid dis.	Digestion 3d. With neutral citrate of ammonia solution, with 1 cc. of ammonia added to each 50 cc. temperature 65° C. Per cent. Phos. acid dis.	Digestion 4th. With neutral citrate of ammonia solution, with 1 cc. of ammonia added to each 50 cc. temperature 65° C. Per cent. Phos. acid dis.	Digestion 5th. With neutral citrate of ammonia solution, with 753 gram citric acid added to each 50 cc. temperature 65° C. Per cent. Phos. acid dis.
1.	Apatite (Canadian)	.30	.56	.39	...	...
2.	Caceres (Spain)	.41	.38	.47	...	...
3.	Cambridgeshire Cops	.56	.85	.44	...	...
4.	Logrosan	.68	.41	.66	...	...
5.	Oruba	1.22	2.09	1.14	...	...
6.	Curacao	1.28	1.35	.95	...	...
7.	Bedfordshire Cops	1.38	1.18	.95	...	...
8.	Fr. Ph'rite, Dept. Lot	1.64	1.88	1.50	...	...
9.	Fr. Ph'rite, Lot-et-Gar	1.88	1.90	1.59	...	...
10.	Sombrero	1.84	2.29	2.00	...	...
11.	Avalo (fine)	1.96	2.12	1.82	...	...
12.	Orchilla	4.63	4.81	3.67	...	...
13.	Bone Black	5.47	6.13	4.00	...	...
14.	Avalo (lump)	5.60	5.83	4.48	...	...
15.	Raza Island (Gulf Cal.)	5.92	6.17	5.71	...	...
16.	Lahn Phosphorite	.82	.76	1.35	...	1.59
17.	Suffolk Cops	2.83	2.73	2.05	...	5.00
18.	Bone Ash	2.97	3.93	2.61	...	5.71
19.	Mona Island	6.47	6.82	5.91	...	9.31
20.	Per. Guano (Tarapaca)	12.74	13.14	11.99	8.98	16.17
21.	So. Carolina (river)	1.09	1.35	1.06	1.06	2.89
22.	Navassa	2.73	2.53	1.86	1.22	4.87
23.	Curacao Guano	6.00	6.19	4.59	3.86	....
Average (No. 1)		2.91	3.17	2.76	...	...
Average (No. 2) (20 to 23 inclusive.)		...	5.80	4.85	3.78	...
Average (No. 3) (16 to 22 inclusive.)		...	4.46	...	...	6.50

Iron and Alumina Phosphates.

No.	Commercial Name.	Per cent. Phos. acid dis.	Per cent. Phos. acid dis.	Per cent. Phos. acid dis.	Per cent. Phos. acid dis.	Per cent. Phos. acid dis.
24.	Grand Connetable	1.16	1.97	5.82	11.44	1.12
25.	El Roque	1.36	1.96	4.27	5.68	...
Average (No. 4)		1.26	1.96	5.04	8.56	1.12

Besides the general interest which attaches to the above table, as showing the relative solubility of the different natural phosphates when treated exactly alike with citrate of ammonia solution, the following points are worthy of consideration:

1. A slight acidity of the solution largely increases the quantity of raw phosphate dissolved, as is shown by average (3).

2. A slight alkalinity decreases, to a marked extent, the solvent action on all phosphates of lime, as is shown by averages (1) and (2).

3. A stronger alkalinity decreases still more this solvent action on phosphates of lime, as is shown by average (2).

4. An alkalinity increases, on the other hand, the solvent power of the citrate of ammonia solution on phosphates, when the phosphoric acid exists as phosphates of iron and alumina, and not as phosphate of lime, as is shown by average (4).

As the aim of the ideal method of determining reverted phosphoric acid is to separate the precipitated phosphates from the original insoluble phosphate still left in a fertilizer, it follows from the above four points that the *neutral* citrate of ammonia solution is decidedly superior to either an acid or ammoniacal solution.

5. A change in the temperature of digestion, from 40° C. to 65° C., increases only slightly the solvent action on natural phosphates, as is shown by average (1); the increase being from 2.91 per cent. to 3.17 per cent.; a difference of only 0.26 per cent.

II.—Experiments on Artificial Soils.

In these experiments, finely ground sand was used to represent the soil mass.

With weighed and separate portions of this were mixed weighed quantities of

(1) Carbonate of lime (freshly precipitated),
(2) Oxide of iron (freshly precipitated),
(3) Oxide of aluminum (freshly precipitated),
(4) Brown[1] hematite (finely ground),
(5) Bauxite[2] (finely ground).

Experiment No. 1.

(*a*) To a mixture of 5 grams fine sand with 0.250 gram of carbonate of lime, was added .200 gram sodium ammonium phos-

[1] Brown hematite comp. $H_6Fe_2O_9$ = sesquioxide iron 85.6 per cent., water 14.4 per cent.
[2] Bauxite comp. perhaps $Al(Fe)O_3 + 2Aq$. Dana.

phate dissolved in water. After exposure in an open vessel and drying in the shade, for 72 hours, in this manner, it was divided into two equal parts and digested in neutral ammonium citrate solution 30 minutes with the following results:

Temperature 40° C., phosphoric acid dissolved .0767 gram; temperature 65° C., phosphoric acid dissolved .0761 gram; showing that the reverted phosphate was completely dissolved at both temperatures.

(*b*) Mixture of 5 grams fine sand; .500 gram precipitated carbonate of lime with solution of .500 gram sodium ammonium phosphate was exposed in an open vessel, *in the sun*, 72 hours. After drying in this manner it was digested with citrate of ammonia solution at temperature 40° C., and all the reverted phosphoric acid was dissolved.

(*c*) A similar mixture, treated in the same manner, except that it was exposed in the shade, gave the same results.

Experiment No. 2.

Conducted in the same manner as Experiment No. 1 (*a*). Mixture 5 grams fine sand, 1 gram freshly precipitated sesquioxide of iron, solution .500 gram sodium ammonium phosphate, containing about .190 gram phosphoric acid. (There was no lime present.)

One-half digested with citrate of ammonia, temperature 40° C., phosphoric acid added and afterwards reverted = .095 gram; reverted phosphoric acid dissolved = .0653 gram.

One-half digested with citrate of ammonia, temperature 65° C., phosphoric acid added and afterwards reverted = .095 gram; reverted phosphoric acid dissolved = .096 gram.

Amount of reverted phosphoric acid not dissolved at 40° C. .0297 gram.

The mixture was tested for soluble and only a trace found.

Experiment No. 3.

Conducted in the same manner as Nos. 1 and 2. Mixture 5 grams fine sand, 1 gram freshly precipitated hydrate of alumina, with solution of .500 gram sodium ammonium phosphate, containing about .190 gram phosphoric acid.

After 72 hours, one-half digested with citrate ammonia, temperature 40° C., phosphoric acid added = .095 gram, reverted phosphoric acid dissolved = .0535 gram. One-half digested with citrate

of ammonia, temperature 65° C., phosphoric acid added = .095 gram, reverted phosphoric acid dissolved = .0943 gram; amount of reverted phosphoric acid not dissolved at 40° C. .0415 gram. The mixture was tested for soluble *and only a trace found.*

Experiment No. 4.

Conducted in the same manner as Experiments 1, 2 and 3. Mixture 30 grams fine sand, 3 grams brown hematite, with solution of .750 gram sodium ammonium phosphate, containing about .261 gram phosphoric acid.

After 72 hours, divided into three equal parts, one-third digested with citrate of ammonia, temperature 40° C., phosphoric acid present = .091 gram, phosphoric acid dissolved = .076 gram, reverted phosphoric acid dissolved = .0503 gram. One-third digested with citrate of ammonia, temperature 65° C., phosphoric acid present = .091 gram, phosphoric acid dissolved = .089 gram, reverted phosphoric acid dissolved = .0633 gram. One-third digested with cold water, phosphoric acid present = .091 gram, phosphoric acid dissolved = .0257 gram, reverted phosphoric acid dissolved = .0653 gram.

Total reverted phosphoric acid present = .0653 gram; amount total reverted phosphoric acid present not dissolved at 40° C., .015 gram.

Experiment No. 5.

Conducted in same manner as Experiments 1, 2, 3 and 4. Mixture 30 grams fine sand, 3 grams bauxite, with solution of .750 gram sodium ammonium phosphate, containing about .261 gram phosphoric acid.

After 72 hours, divided into three equal parts, one-third digested with citrate of ammonia, temperature 40° C., phosphoric acid present = .091 gram, phosphoric acid dissolved = .080 gram, reverted phosphoric acid dissolved = .0457 gram. One-third digested with citrate of ammonia, temperature 65° C., phosphoric acid present = .091 gram, phosphoric acid dissolved = .0915 gram, reverted phosphoric acid dissolved = .0571 gram. One-third digested with cold water, phosphoric acid present = .091 gram, phosphoric acid dissolved = .0344 gram, reverted phosphoric acid dissolved = .0566 gram.

Total reverted phosphoric acid present = .0566 gram; amount total reverted phosphoric acid present not dissolved at 40° C., .0109 gram.

Experiment No. 1 (*a*, *b*, *c*) shows that ammonium citrate solution at 40° C. dissolved all the reverted phosphates of lime.

Experiment No. 2 shows that at temperature of 65° C. ammonium citrate solution dissolved all the reverted phosphate of iron present, while at temperature of 40° C. it failed to dissolve 31.26 per cent. of the phosphoric acid actually reverted.

Experiment No. 3 shows that at temperature of 65° C. ammonium citrate solution dissolved all the reverted phosphates of alumina present, while at temperature of 40° C. it failed to dissolve 43.68 per cent. of the phosphoric acid actually reverted.

Experiment No. 4 shows that at temperature of 65° C. ammonium citrate solution dissolved all the reverted phosphate present, while at temperature of 40° C. it failed to dissolve 22.68 per cent. of the phosphoric acid actually reverted.

Experiment No. 5 shows that at temperature of 65° C. ammonium citrate solution dissolved all the reverted phosphate present, while at temperature of 40° C. it failed to dissolve 17.49 per cent. of the phosphoric acid actually reverted.

III.—Experiments on Natural Soils.

The soils used were light loams; one from the truck gardens of Long Island, N. Y., one from the cotton plantations of North Carolina, and one from the tobacco fields of Connecticut; taken from plots upon which fertilizers have been sown and large crops of the above staples grown.

The soils were ground to pass through a 20 mesh sieve, and 100 grams of each were weighed for each experiment.

160 grams of an ammoniated superphosphate were digested in 2 liters of water and filtered; the quantity of phosphoric acid found by analysis in 50 cc. of this filtrate was .284 gram. This quantity was added to 100 grams of each soil as prepared above, and the mixture was stirred to a thin, wet, pasty condition; allowed to remain five days in thin layer, exposed to the open atmospheric conditions, in the shade, in open vessels; at the end of this period they were weighed and divided into four equal parts for digestion in citrate of ammonia solution, at temps. 40° C. and 65° C., and with water, to determine amount not reverted.

In order to calculate the exact quantity of reverted dissolved by these digestions, the amount originally in each soil was estimated by previous digestions as follows:

Soil.	Amount Phosphoric Acid dissolved from 25 grams by Citrate of Ammonia, temperature 40° C.	Amount Phosphoric Acid dissolved from 25 grams by Citrate of Ammonia, temperature 65° C.	Amount Phosphoric Acid dissolved from 25 grams by water.
No. 1. Long Island garden,	.0193 gram	.0292 gram	trace
2. North Carolina cotton,	.003	.0076	"
3. Connecticut tobacco,	.0072	.0163	"

Corrections have been made, according to the above results, in the following tables:

Soil Experiment No. 1.—Long Island Garden Soil.

25 gram mixture, digested with citrate of ammonia, temperature 40° C., phosphoric acid added = .071 gram; phosphoric acid dissolved = .0532 gram; reverted phosphoric acid dissolved = .0462 gram.

25 gram mixture, digested with citrate of ammonia, temperature 65° C., phosphoric acid added = .071 gram; phosphoric acid dissolved = .0702 gram; reverted phosphoric acid dissolved = .0632 gram.

25 gram mixture, digested with water, phosphoric acid added = .071 gram; phosphoric acid dissolved = .007 gram; reverted phosphoric acid dissolved = .064 gram.

Amount of phosphoric acid added, actually reverted = .064 gram; amount phosphoric acid added, actually reverted and not dissolved at 40° C. = .0178 gram.

Soil Experiment No. 2.—North Carolina Cotton Soil.

25 gram mixture, digested with citrate of ammonia, temperature 40° C., phosphoric acid added = .071 gram; phosphoric acid dissolved = .053 gram; reverted phosphoric acid dissolved = .0468 gram.

25 gram mixture, digested with citrate of ammonia, temperature 65° C., phosphoric acid added = .071 gram; phosphoric acid dissolved = .0713 gram; reverted phosphoric acid dissolved = .0651 gram.

25 gram mixture, digested with water, phosphoric acid added = .071 gram; phosphoric acid dissolved = .0062 gram; reverted phosphoric acid dissolved = .0648 gram.

Amount of phosphoric acid added, actually reverted = .0648 gram; amount of phosphoric acid added, actually reverted and not dissolved at 40° C. = .018 gram.

Soil Experiment No. 3.—Connecticut Tobacco Soil.

25 gram mixture, digested with citrate of ammonia, temperature 40° C., phosphoric acid added = .071 gram; phosphoric acid dissolved = .052 gram; reverted phosphoric acid dissolved = .046 gram.

25 gram mixture, digested with citrate of ammonia, temperature 65° C., phosphoric acid added = .071 gram; phosphoric acid dissolved = .0698 gram; reverted phosphoric acid dissolved = .0638 gram.

25 gram mixture, digested with water, phosphoric acid added = .071 gram; phosphoric acid dissolved = .006 gram; reverted phosphoric acid dissolved = .065 gram.

Amount of phosphoric acid added, actually reverted = .065 gram; amount of phosphoric acid added, actually reverted and not dissolved at 40° C. = .019 gram.

Experiment No. 1 shows that citrate of ammonia solution at temperature of 65° C. dissolves all the phosphoric acid added to the soil, while at temperature 40° C. it fails to dissolve 27.81 per cent. of the phosphoric acid actually reverted by the soil.

Experiment No. 2 shows that citrate of ammonia solution at temperature of 65° C. dissolves all the phosphoric acid added to the soil, while at temperature of 40° C. it fails to dissolve 27.77 per cent. of the phosphoric acid actually reverted by the soil.

Experiment No. 3 shows that citrate of ammonia solution at temperature 65° C. dissolves all the phosphoric acid added to the soil, while at temperature of 40° C. it fails to dissolve 29.23 per cent. of the phosphoric acid actually reverted by the soil.

In order to obtain a thorough and uniform mixture of the solution of phosphoric acid with so large a volume of soil, the mass was made very wet and stirred. During two days its condition represented very wet lands; later, as more water evaporated, it took upon itself all the successive stages of drouth, but at no time contained less moisture than was observed in the fields from the surface to depths varying several inches during the summer season. Tests made with other portions of these mixtures showed that all the phosphoric acid was dissolved at both temperatures, if kept constantly saturated with water, owing to the ready solubility of all gelatinous precipitates at low temperatures.

Whether phosphoric acid exists in the soil in combination with lime only, or also with iron and alumina, has heretofore never

been proven by any direct laboratory tests, because no method of separation was known for distinguishing these three phosphates in the presence of each other in the soil. The results of soil experiments 1, 2, 3 (pp. 4, 5) show that advantage can be taken of this discovery to formulate a method of a laboratory qualitative test for reverted iron and alumina phosphates, under the above conditions. The fact that a strongly alkaline citrate of ammonia solution rapidly attacks insoluble iron and alumina phosphates, but dissolves even less of insoluble lime phosphate than when neutral, constitutes another test for distinguishing these phosphates.

Many investigators have sought a direct proof since the work of Thénard[1] on this subject, but I am not aware that any has been found.

That phosphoric acid becomes reverted, or insoluble in water, when in contact with soil, has been demonstrated by many experiments by such noted scientists as Bronner,[2] Thompson and Huxtable,[3] Way,[4] Liebig,[5] Mulder,[6] Knop and Hussakowsky,[7] Salomon,[8] Millot,[9] Joullie,[10] Voelcker,[11] and in our own country by Drs. Johnson[12] and Shepard.[13]

Of these, a large number believed that it becomes combined largely with iron and alumina. Knop especially proved that phosphoric acid was fixed in greater amount, and more rapidly, when oxides of these bases were *added* to soils, and that soils containing *large quantities* had greater reverting properties than those containing *less* oxides of iron and alumina.

Thénard and Déhérain discussed elaborate theories to establish the chemical reaction by which plants could absorb phosphoric acid from its combinations with iron and alumina; but experience has taught the agriculturist that he cannot reason with certainty regarding these intricate processes.

That plants do absorb phosphoric acid from pure phosphate of iron and alumina, by *some means*, has been demonstrated beyond a doubt in recent field experiments by Drs. Peterson,[14] Voelcker,[15]

[1] Comptes Rendus, 1856, 46, 212.
[2] Treatise 1836, and Jahresbericht der ag. Chemie, 1863-64, 6.
[3] Roy. Ag. Soc. Jour. Eng.
[4] *Ibid.* 1850, **11**, 313; **15**, 91.
[5] Annalen der Chemie und Physik, **105, 106.**
[6] Chemie der Akerkrume, **1**, 465.
[7] Knop's Agric. Chemie.
[8] *Ibid.* **2**. 177.
[9] Annales Agronomique, 1880; Barrel, Jour. d'Agric. 1879.
[10] Comptes Rendus, 1879, 1324.
[11] Roy. Ag. Soc. Jour. Eng. 1862, and **1**, 1, p. 37.
[12] How Crops Feed; and Rpts. Conn. Ag. Soc.
[13] Rural Carolinian, June, 1872.
[14] Fühling's Landwirthschaft. Zeitung, 1876, **5**, 336.
[15] Royal Ag. Soc. Jour. **31**, 1880, 152; **33**, 1881, and **34**, 1882.

Fittbogan,[1] Prof. Dietrich,[1] F. Oldenberg,[1] Renow,[1] and Dr. Birner,[1] Prof. Maercker,[2] Hoffmeister,[3] and others.

Leaving the theoretical discussion of this question, the practical view of the case is best expressed in the following words from Prof. S. W. Johnson's work, "How Crops Feed" (p. 374): "The great beneficent law regulating these absorptions appears to admit of the following expressions: those bodies which are most rare and precious to the growing plant are by the soil converted into and retained in a condition not of absolute, but of relative insolubility, and are kept available to the plant by the continual circulation in the soil of the more abundant saline matters."

The quantities of iron and aluminum oxides introduced into the mixtures of artificial soils, with which Experiments 2, 3, 4, 5 (pp. 5, 6) were performed, were chosen according to the average amount of these oxides in soils.

Analyses of 87 soils, collected from all the farming districts of New York State by Emmons[4] in 1846, show the average contents of iron oxide and alumina to be 7.79 per cent.; of lime, 0.84 per cent.

The average of 20 representative soils, collected in New Jersey by Cook,[5] shows by analysis, oxide of iron and alumina 19.33 per cent.; lime 0.77 per cent.

And even in Ohio, where the geological formation is lime rock, the soils contain much more of these oxides than of lime. The average of 13 representative soils shows by analysis,[6] oxide of iron and alumina 3 per cent.; lime 1.25 per cent.

Very many soils contain less than 0.15 per cent. of lime. The normal amount, it is safe to say, does not exceed 0.45 per cent. Lime is rapidly removed from soils by percolating waters. In formations of lime rock, huge caverns are formed by this process; whereas the iron and alumina of the rocks remain in the soils formed from them, with a consequent increase of the relative proportions between these bases and lime.

Knop,[7] Salomon[8] and others have shown that this loss of lime is also largely due to reactions in the soil, by which soluble compounds of lime are formed with nitric, sulphuric, muriatic and humic acids.

[1] Biedermann's Centralblatt, March, 1881, 156.
[2] *Ibid.* June, 1881, 378.
[3] *Ibid.* Dec. 1881, 813.
[4] Geol. Report New York State, 1846.
[5] *Ibid.* New Jersey, 1869.
[6] *Ibid.* Ohio, 1870.
[7] Knop's Ag. Chemie, 2, 177.
[8] *Ibid.*

Albert and Vollbrecht[1] experimented on soils containing a large amount of lime, and with others containing a small amount, with the results here given in abstract:

They mixed 10 grams soil, containing 18.1 per cent. carbonate of lime; 2.5 grams superphosphate, containing 9.3 per cent. phosphoric acid, soluble in water, and 12.06 per cent. reverted, soluble at temperature 40° C. in neutral solution of citrate of ammonia. Of the total phosphoric acid present,

	After hours.			Days.				
In the shade, there became insoluble in water,	4	8	12	3	6	8	10	14
	Per cent.			Per cent.				
	78	88.4	90.2	91.1	91.7	93.4	93.8	95
There became insoluble in citrate of ammonia at temperature 40° C.,				2.1	3	4.1	4.1	4.1
In the sun, there became insoluble in water,				97.4	...	100	...	...
In citrate of ammonia at 40° C.,				4.6	...	6.6	...	...

Soil containing small amount of lime mixed with the same superphosphate; of total phosphoric acid present,

	After hours.		Days.				
There became insoluble in citrate of ammonia at 40° C.,	12	14	3	4	8	10	14
	Per cent.		Per cent.				
	3.1	4.7	4.7	5.8	6.5	6.5	6.8

In another experiment they mixed 10 grams soil rich in lime, 2 grams superphosphate, containing soluble phosphoric acid 27 per cent., reverted, at 40° C., 21.7 per cent. Of total phosphoric acid present,

	After days.					
There became insoluble in citrate of ammonia at 40° C.,	3	5	6	8	10	14
			Per cent.			
In the shade,	4.1	5.4	5.4	...	6.8	7.4
In the sun,	11.1	...	...	15.4	...	...

In another experiment they mixed 10 grams clay soil, 2 grams superphosphate above used. Of the total phosphoric acid present,

	Days.		
There became insoluble in the shade, in the citrate of ammonia, temperature 40° C.,	3	8	14
	Per cent.		
	8.2	12.1	...

In another experiment with a sandy soil, same mixture. Of the total phosphoric acid present,

	Days.		
There became insoluble in citrate of ammonia, temperature 40° C., in the shade,	3	8	14
	Per cent.		
	4.	5.2	7.1

[1] Biedermann's Centralblatt, Feb. 1880, 84.

The authors, with Millot and Joullie, concluded from these experiments that the amount of phosphoric acid not dissolved by citrate of ammonia solution at 40° C. had become *insoluble phosphate of lime;* and so Déhérain[1] thought possibly oxide of iron and alumina produce insoluble phosphate of lime.

Had they digested these soils at the *temperature of* 65° C. *these discrepancies would have disappeared,* as is shown by experiments on soils 1, 2 and 3 (pp. 4, 5).

If all the reverted phosphoric acid present in these experimental mixtures had been in combination with lime, it would have been entirely redissolved at temperature 40° C. by the neutral citrate of ammonia solution, as is proved by Experiment No. 1 (p. 3), where lime was the only base present.

Therefore it is impossible to draw any other conclusion than that a portion of the phosphoric acid added was in *combination as reverted phosphates of iron and alumina in these soils.*

Thénard and Déhérain in 1858 believed that when even insoluble phosphate of lime was applied to the soil, eventually the phosphoric acid became combined with iron and alumina, through the chemical agencies of soils.

The physical conditions of oxide of iron and alumina in soils do not seem to affect the principal result of these comparisons of temperatures at which citrate of ammonia solution is used. The mineral brown hematite, used in Experiment No. 4 (p. 6), was chosen to represent the mineral oxides of iron formed by the decomposition of rocks; though much more active forms of these oxides, such as proto-compounds, are supposed to be present in the chemical changes going on in soils. Bauxite, used in Experiment No. 5 (p. 6), represents in the same manner the possible condition of alumina in soils. In short, I do not think that these minerals can be *more active* in their affinities for phosphoric acid than are those contained in soils.

Few deposits of mineral phosphates exist which are not contaminated with oxide of iron and alumina. Vast stores of phosphoric acid, provided by Nature for agricultural use, are represented by the following names of deposits:

[1] Annales Agronomique, Dec. 1880.

Commercial Name.[1]	Per cent. contents oxide iron and alumina.
Wicken Coprolites,	12.00
Cambridgeshire Coprolites,	3.25 to 5.25
Bedfordshire "	8.00 to 10.00
Ardennes "	not mentioned
Grand Pré "	"
Suffolk "	4.75 to 10.50
Varennes, "	not mentioned
Bellegarde "	"
Boulogne "	6.00 to 11.50
Bordeaux "	4 to 13
German Phosphorites,	4.5 to 15
Russian "	6
Spanish "	1.25 to 4
Oruba "	14.5 to 26.50
Navassa Red,	10 to 25
" Lower Flat,	4 to 12
Sombrero,	4 to 10
St. Martin's,	2.75 to 4.50
Malden Island,	1
South Carolina (land)	7

The last is now sold in market, colored a pronounced reddish tint by the oxide of iron it contains. It is evident that superphosphates made from such minerals are undervalued when the reverted phosphoric acid is estimated at a temperature of 40° C.; because, as is fair to conclude from Experiments 2, 3, 4 and 5 (pp. 5, 6), the oxides dissolved by the sulphuric acid subsequently combine in the superphosphate with their equivalent of phosphoric acid, and the reverted phosphates of iron and alumina thus formed are not *all dissolved at the temperature of* 40° C.; whereas, a slight increase in temperature dissolves them entirely, without unduly attacking the *insoluble* mineral, as is proven by my experiments on raw phosphates (p. 3).

Millot[2] showed the result of contact of these oxides with soluble phosphates in a superphosphate prepared from coprolites of the Ardennes. All the phosphoric acid was soluble in water when freshly made, but after two years 90 per cent. of the phosphoric acid was insoluble in water. Millot washed this with hot water until

[1] Spons' Encyc. [2] Comptes Rendus, **78**, 1134; **82**, 522.

all the gypsum was removed, and found the residue to be *free from lime* and to consist of phosphate of iron.

The experiments of Dr. E. Heyden[1] show how very rapidly and completely reversion takes place under conditions more nearly similar to those when fertilizers are applied to fields. He filtered solutions containing an equal amount of phosphoric acid through four separate soils; 2500 cc. of the solutions to each 1250 grams of the soils.

	Amount Reverted.	Amount Soluble.	Per cent. not Reverted.
Soil A, surface soil within 8″ of surface.	.137 gram	.0057 gram	4.16
Soil A, subsoil, between 8″ and 16″.	.147	.0026	1.76
Soil B, surface, within 8″ of surface.	.165	.0053	3.21
Soil B, subsoil, between 8″ and 16″.	.153	.0019	1.24

Dr. Stohman[2] showed by his experiments that from a *dilute* solution of salts, filtered through a given mass of soil, a larger per cent. was removed than from a more concentrated solution. One thousand pounds of superphosphate, containing one hundred pounds of soluble phosphoric acid, sown upon an acre of land, represent a distribution of only 0.0005 gram to every 26.7 grams of soil, which is the weight of a mass 1 sq. inch in surface and 3 inches deep. In the experiments of Heyden, just quoted, 0.150 gram P_2O_5 was used to 1250 grams of soil, or about 0.0035 gram to every 26.7 grams of soil. In my experiments 0.071 gram P_2O_5 was used to 25 grams of soil. Thus in actual field practice a solution is employed which, proportionately to the soil, is seven times more dilute than that which Heyden experimented with, and about one hundred and twenty times more dilute than that used in my experiments. It is probable, therefore, that the superphosphate becomes reverted *on the spot* where it is sown. If spread broadcast, it lies near the surface; if harrowed or plowed under, it is brought a few inches deeper. Liebig[3] analysed samples of soil at the experiment station at Rothamsted which had received dressings of superphosphates for twenty-two years in succession, and found three-fourths of the phosphoric acid in the first nine inches of soil.

[1] Annalen der Landwirthschaft, **45**, 189. [2] Henneberg's Jour. f. Landwirthschaft, 1862.
[3] Roy. Ag. Soc., June, 1881.

In conclusion, it is evident, from the *marked* and *positive* results of the foregoing experiments, that the only *equitable* method of valuation of the *reverted phosphoric acid* of a *superphosphate* must be based upon these facts.

I assert, therefore, that the true method of analysis is that which dissolves reverted phosphates of the same degree of solubility as those which are formed when a soluble superphosphate is mixed with the soil;

That the value of a superphosphate is determined, not alone by its condition in the storehouse, but by its condition within a reasonable time after being sown upon the field;

That phosphates, soluble in water, become, within a few hours, entirely reverted in some cases, in others to the extent of over 90 per cent. This has been shown by my experiments with artificial and natural soils; and there is no lack of testimony by most eminent authorities in verification of these results;

That a superphosphate which was valued by a method in which the temperature was 40° C., if re-analysed by the same temperature after several days' contact with the soil, would show, after allowing for the amount previously in the soil, an apparent loss of 20 to 30 per cent. of available phosphoric acid, as has actually been shown by Experiments 1, 2 and 3 (pp. 8, 9).

The following method of analysis of superphosphates recognises the principles demonstrated in this and the previous papers, and contains in addition a detailed manipulation which long experience has fully recommended to our confidence.

Method of Analysis of Superphosphates.

Preparation of Sample.—Pass the sample[1] through a twelve-mesh sieve.

Moisture.—Dry 5 or 10 grams at 100° C.

Total Phosphoric Acid.—Weigh 2 grams, brush into a 200 cc. flask, add 50 cc. nitric acid,[2] boil gently for 15 minutes, cool, fill to mark, mix, filter through a dry filter-paper into a dry receiver, take 50 cc. of filtrate, place in a beaker, add 25 cc. conc. ammonia, then nitric acid to acidity. To the hot liquid add *molybdic solution*, let stand

[1] If too wet, a portion of the sample must be air-dried and then sifted, and an allowance made by calculation for loss of moisture.

[2] Several cubic centimeters of HCl must be added here, and in solution of the insoluble when working with difficultly soluble iron and alumina phosphates.

for one hour at about 65° C., filter, wash with *nitrate of ammonia* solution, dissolve on paper with hot *ammonia solution*, and wash with same. Run in *magnesia mixture* from a burette at the rate of one drop a second, stirring constantly. Let stand several hours, filter, wash with *ammonia solution*, dry, ignite to whiteness and weigh.

Soluble Phosphoric Acid.—Weigh 2 grams, rub up in a mortar with a soft *rubber-tipped* pestle,[1] digest in 25 cc. of cold water, decant clear liquid into a filter-paper, filtering into a 200 cc. flask, add 25 cc. of water to residue, digest for several minutes and again decant. Repeat for five or six times, and finally bring all upon the filter-paper and wash till flask is filled to the mark. Mix, take 50 cc. and estimate P_2O_5 as in total.

Insoluble Phosphoric Acid.—Wash the residue upon the paper into a 200 cc. flask with 100 cc. *citrate solution*, cork the flask with a common cork, digest in a water-bath at constant temperature 65° C. (150° F.) for thirty minutes, with frequent agitation. Filter the warm solution quickly,[2] and wash with cold *water*. Return paper and contents to the same 200 cc. flask, add 50 cc. nitric acid, boil for fifteen minutes and estimate the P_2O_5 as in total.[3]

Reverted Phosphoric Acid.—The soluble + insoluble phosphoric acid subtracted from the total will give the reverted phosphoric acid.

Memoranda.

Molybdic Solution.—This is made up as usual to contain 5 per cent. MoO_3. Of this use 60 cc. to every 0.100 gram P_2O_5. (The filtrate should be tested by addition of phosphate soda, to see that an excess of precipitant is employed.)

Magnesia Mixture.—Make up as follows:

110 grams cryst. magnesium chloride,
300 grams ammonium chloride,
400 cc. conc. ammonia,
1500 cc. water.

[1] This serves simply to break up lumps. No grinding nor trituration of sample is made either in extraction of soluble or reverted phosphoric acid.

[2] This is best accomplished by use of a filter-pump, or by use of plaited filter-paper. After the citrate solution has run through, the first paper may advantageously be rolled up, placed upon a second paper and washed. The use of citrate solution for washing is discarded as being equivalent to further treatment.

[3] The organic matter from the paper does not interfere in the least with the estimation. We have never found soluble silicic acid in any phosphate in sufficient quantity to give a precipitate and thus interfere with the accuracy of the above method.

Use 10 cc. to every 0.100 gram P_2O_5.

(15 cc. added to 100 cc. *ammonia solution;* must remain clear after standing twenty-four hours.)

Citrate Solution.—Made up to sp. gr. 1.09 carefully neutralised.

Ammonia Solution.—This consists of one part strongest ammonia to three parts water.

Nitrate of Ammonia Solution.—This is a 10 per cent. nitrate of ammonia solution slightly acidified with nitric acid.

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THE DETERMINATION OF THE FLASHING POINT OF PETROLEUM.

BY JOHN T. STODDARD.

In a recently published paper[1] on this subject, Beilstein reviews the method proposed by me last year,[2] and reaches some conclusions so different from mine that I have been led to repeat my former experiments and to subject the method to a still more thorough investigation.

The method is a modification of that due to Liebermann,[3] and consists in testing a mixed current of air and petroleum vapor, obtained by forcing air through petroleum, as it issues from the mouth of a cylindrical oil holder. Having found that a continuous current of air gives results which are nearly identical with those obtained by the intermittent current employed by Liebermann, I proposed the substitution of the former on account of the greater uniformity of the results and the increased simplicity of manipulation. Beilstein concludes from his experiments with the tester that the use of a continuous current of air "must lead to entirely wrong results," as, he writes, Liebermann had already pointed out. It is, however, noteworthy that while Liebermann[4]

[1] Zeitschrift für analytische Chemie, **22**, 309.
[2] This Journal, **4**, 285.
[3] Zeitschrift für analytische Chemie, **21**, 321.
[4] *Loc. cit.*

foregoes the use of the continuous current because he finds from his experiments that it *raises* the flashing point, Beilstein's objection to it is that it gives *too low* a result.

Two series of experiments are given as the basis of this conclusion. In one series the sample of oil was kept at a constant temperature, while air was forced through it and a small flame held at the mouth of the cylinder until the flash took place, if at all. The results obtained are:

Time before flash,	3 sec.	5	6	8	11	41
Temperature of oil,	29.1°	28.7	28.3	27.8	27.2	26

At 25.3° no flash occurred, even after six minutes.

In consequence of this evident dependence of the result upon the duration of the air current, five seconds was chosen as the normal (?) time in the second series of experiments, which show that the oftener the test is repeated, *i. e.* the more air that is led through the oil while it is heated, the lower is the temperature at which the flash takes place. Oil which on direct heating did not flash below 28.7° was tested through different ranges of temperature by leading air and holding the flash jet at the mouth of the holder for five seconds at each degree, with the following results:

Beginning at	11°	12	18	24	26	27
Oil flashed at	27.3°	27.2	27.7	28.3	28.2	28.7

My experiments on the influence of duration of air current on the flashing point confirm the results given by Beilstein; but at the same time show that the interpretation of them which leads him to the arbitrary choice of a normal interval is quite gratuitous. It will be noticed in the results which he gives, that the lower the temperature at which the oil is held, the longer is it necessary to continue the air current in order to obtain a flash, until finally at 26° a minimum flashing point is reached, below which no flash is obtained even after six minutes; and this too in spite of the demonstration which follows in the second series of results that the flashing point is lowered by increasing the quantity of air led through the oil.

My results, some of which are given below, also indicate clearly that a minimum is reached after the air has run through the oil thirty to sixty seconds; while further experiments (see II) show unmistakably that longer continuance of the air tends to slowly *raise* the temperature at which the oil will flash.

I. *Influence of duration of air current on the flashing point of oil held at a constant temperature.*

1. Time before flash,	3 sec.	30	55	35	42	60[1]	82[1]	no flash.
Temperature of oil,	36.8°	36.2	36	36	36	35.9	35.7	35.4
2. Time before flash,	27 sec.	30		48		65	36	no flash.
Temperature of oil,	36°	35.7		35.6		35.6	35.6	35.4
3. Time before flash,		15 sec.		60		40		no flash.
Temperature of oil,		28.3°		27.6		27.6		27.2

II. *Influence of quantity of air led through the oil as it is heated.*

1. Time of continuous air current,	2.5 min.	3	5	12
Flashing point, ...	35.3	35.4	35.5	36.3

2. Air led for 5 sec. at each degree, and when near the flashing point every 0.2°–0.3° :

Beginning at,	45°	40	36	27	16
Flashing point,	47.6°	47.7	47.4	47.8	48

These last results lead, as has already been indicated, to an opposite conclusion from that reached by Beilstein. That a higher flashing point should be the result of increasing the quantity of air led through the oil is, however, what one would naturally expect; for the more volatile portions are being continually removed by the air current—more rapidly, of course, as the temperature rises—and thus the flash must occur at a higher point, unless the amount of oil with respect to that of air is large.

In none of the experiments which Beilstein gives on this point, however, can the quantity of air have been large enough to appreciably raise the flashing point, as is shown by II (in the determination which began at 11° and resulted in a flash at 27.3° the air is equivalent to a continuous current for $18 \times 5 = 90$ sec.); and the only explanation of his figures, it seems to me, must be found in the irregularity of the results which, in my experience, always attends the use of the intermittent method. This irregularity of results, and also the fact that the intermittent method gives higher flashing points than the continuous—which, indeed, is evident from I.—is shown by the following.

[1] After several abortive flashes which heated the sides of the holder.

III. *Comparison of the intermittent and continuous methods.*[1]

Flashing points determined by the

	1.	2.	3.
5 sec. method, . .	47.7°	36.8, 37	37.1, 36.8, 36.5, 36.6, 36.8
Continuous method,	46.4	35.6, 35.7, 35.7	36.1

I am also unable to agree with the interpretation which is given of experiments with oil cylinders of different dimensions. Everything depends, according to Beilstein, on the ratio of diameter to length of cylinder. Concordant results can only be obtained when the length is 5–7 times the diameter. If these limits are observed, it makes no difference to what height the cylinder is filled with oil.

It will be seen by reference to the determinations given below, that the flashing point depends, not upon the dimensions of the *cylinder*, but upon the dimensions of the *vapor space* above the surface of the oil. Cylinders of the same diameter and different lengths all give the same flashing point when filled to the same distance from the top. Indeed, this follows as a necessary corollary to the fact established by Liebermann,[2] that the quantity of oil does not affect the determination; for difference in length of cylinder in this case means simply difference in the quantity of oil employed in the test.

IV. *Determinations made in cylinders of different dimensions.*

"Vapor space" = distance from foam to mouth of cylinder.

1. Vapor Space.	Dimensions of Cylinders.				
	2 × 10 cm.	2 × 16	2 × 20	2 × 30	2 × 40
5 cm.	32.7°	32.8	32.7	32.6	32.5
9		33.5	33.5	33.5	33.6
15			34	33.7	34
20				35	34.9 34.6

2. Vapor Space.	Dimensions of Cylinders.			
	3 × 12 cm.	3 × 18	2.7 × 32	3 × 43
7 cm.	35.7°	35.7	35.7	35.9
12.5		36.8	36.6	36.2
18			36.9	36.7

[1] Cf. also this Journal, *loc. cit.*

[2] *Loc. cit.*

V. *Influence of length of vapor space.*[1] 1. Cylinder 3 × 43 cm.

Vapor space,	4 cm.	7	11	15	18	19	25	30	33	36	38
Flashing point,	35.9°	36.3	36.7	37.1	37.2	37	37.6	38.4	38.2	39	39.8

2. Cylinder 4.7 × 25 cm.

Vapor space,	5 cm.	6.5	9.5	13	18
Flashing point,	43.5	43.8	44.3	45	47

VI. *Comparison of results obtained from cylinders of different diameters.* Vapor space in each case 5 cm.

Diameter,	2 cm.	2.7	3	4	4.7	6.5
Flashing point,	43.4° 43.6	43.2	42.8	43.1	42.9	43

The flashing point rises as the distance from the top of the foam to the mouth of the cylinder is increased. Diameters greater than 2.5 cm. scarcely affect the determination when this distance is less than 6 cm. The quantity of oil must not be too small, else the results will be unreliable—higher and somewhat irregular—on account of loss of vapor carried away by the air current before the flashing point is reached. My recent investigation has led me to fix 50 cc. as the minimum quantity of oil which should be used for a determination. The cylinder which serves as oil holder must, therefore, be large enough to contain at least this quantity of oil, and leave a distance of some 6–4 cm. for vapor space. With this larger quantity of oil a stronger current of air than that previously recommended is necessary, and I agree with Beilstein that the current should be strong enough to maintain at least 1 cm. foam on top of the oil.

The aim of this method of testing is to find the *lowest* flashing point which can be accurately determined. It is the outgrowth of the valuable suggestion of Victor Meyer,[2] who thought by saturating air with petroleum vapor to determine the "absolute flashing point"; and although it cannot, perhaps, be claimed that this is accomplished, we certainly have in the method a means of near approximation to this point.

The obvious importance of obtaining a minimum flashing point appears to have been entirely overlooked by Beilstein, who seeks only for concordant results, and, in the modification he proposes, takes as the flashing point a temperature higher than that given by the preliminary test.

[1] Cf. also this Journal, *loc. cit.*

[2] Wagner's Jahresbericht, 1879, 1175.

In the practical employment of a method for testing the safety of petroleum, it is also in the highest degree important that the determination be free, as far as possible, from arbitrary conditions, and that both apparatus and manipulation be of such simplicity that reliable results can be obtained without the necessity of especial skill or experience. It is believed that the apparatus and method described below leave little to be desired in these essential particulars.

1. The oil cylinder should have a diameter of at least 2.5 cm. A diameter of more than 4 cm. is not advisable, because of the large quantity of air which is then required in making the determination (cf. 4). The cylinder may have any convenient length, provided it holds, when filled for the test, not less than 50 cc. of oil. With 2.5 cm. diameter the length should be at least 16 cm.

2. The cylinder is filled with oil to a point such that, when the air is running, the surface of the foam is about 5 cm. from the top.

3. The oil holder is heated in a water-bath in which it sinks to the level of the oil. The temperature should not rise, when approaching the flashing point, faster than 2° a minute.

4. Air is forced through the oil with such velocity that not less than 1 cm. foam is maintained on its surface, and a flash jet brought to the mouth of the cylinder for about one second every 0.5° or oftener in the vicinity of the flashing point. The approach of the flashing point is announced by the appearance of a blue halo of burning vapor about the flame, which is larger at each trial until at last it detaches itself from the flash jet and runs down to the surface of the oil.

The test is now repeated with a fresh sample of the oil, and the air current started not less than one and not more than three to four minutes before the flash. It is a good plan to let a very slow current of air bubble through the oil from the time the tester is put into the water-bath, so as to secure regularity in the heating.

I have usually employed as flash jet a gas flame from the tip of a blowpipe, and about 0.5 cm. long. The size of the flame makes, however, very little difference in the results.

All the temperatures given are in centigrade degrees, and all the determinations were made with a thermometer graduated in 0.2°.

Smith College Laboratory, Northampton, Mass., *Nov. 17th*, 1883.

HAYDENITE.

By H. N. Morse and W. S. Bayley.

Haydenite, which is found in the gneiss quarries near Baltimore, where it is associated with beaumontite and stilbite, was first discovered by Dr. Hayden of Baltimore.

Cleaveland[1] afterwards described it, though apparently with considerable hesitation, as an independent species, and gave to it the name of the discoverer. In consequence of its resemblance to chabazite, however, its independence as a species was generally doubted, until Levy[2] examined the mineral crystallographically, and found it, as he supposed, to be monoclinic. Levy was afterwards shown to be in error by J. D. Dana,[3] who ascertained that the crystallisation of haydenite is in reality rhombohedral, and that the crystals are scalenohedrons. On crystallographic grounds, as well as from a consideration of the physical properties, Dana concluded that haydenite and chabazite are identical, notwithstanding the fact that the analytical results thus far recorded could not be reconciled with this view. The probability of the identity of the two has been further strengthened by the results of the recent optical examination of haydenite by Des Cloizeau.[4]

Up to the present time two analyses of haydenite have been published—one by B. Silliman, Jr.,[5] the other by Delesse.[6] The results obtained differ very widely, and are in neither case reconcilable with what is generally believed to be the typical composition of chabazite.

Under the circumstances it seemed quite desirable that further chemical analyses of the mineral should be made, and having at our disposal a quantity of apparently undecomposed material, we have carefully determined the various constituents. It was found on making a qualitative examination of different specimens, that barium is a constant constituent of the mineral—a fact which had escaped the observation of those who have previously analysed it.

[1] Mineralogy, 2d ed. 478. [2] L'Institut, 1839, **313**, 455; Berzelius' Bericht, **20**, 217.
[3] Am. Journal of Science, (2) **17**, 82.
[4] Bulletin Soc. Min. de France, 1881; Jahrbuch für Min. u. s. w., 1883, 6.
[5] Am. Journal of Science, **46**, 379.
[6] Revue Industr. et Scient. **25**, 107; Berzelius' Bericht, **27**, 248.

We give below the results obtained by Silliman and Delesse, and, afterwards, those found by ourselves:

	Silliman.	Delesse.	
Silica,	56.831	49.5	
Alumina,	12.345	23.5	Al_2O_3
Ferrous oxide,	8.035		Fe_2O_3
Lime,	8.419	2.7	
Magnesia,	3.960	trace	
Potash,	2.388	2.5	
Water,	8.905	21.0	
	99.882	99.2	

	I.	II.	Average.
SiO_2,	49.29	49.19	49.24
Al_2O_3,	18.06	18.07	18.07
Fe_2O_3,	0.79	0.88	0.84
CaO,	5.13	5.19	5.16
MgO,	0.86	0.86	0.86
BaO,	1.46	1.48	1.47
MnO,	trace	trace	...
K_2O,	3.16	2.84	3.00
H_2O,	21.31	21.31	21.31
	100.07	99.81	99.95

If we suppose the small amount of iron found in these analyses to be in the ferrous condition, and therefore, like magnesium and barium, as replacing calcium, and remember that the alkali in chabazite varies within quite wide limits, we find that the results obtained agree with the formula of Rammelsberg for chabazite, quite as closely as those of the more reliable recorded analyses of that mineral. We believe, therefore, that haydenite is in its chemical composition, as well as in its crystallisation and physical properties, identical with chabazite.

Chemical Laboratory, Johns Hopkins University.

Contributions from the Sheffield Laboratory of Yale College.

XVII.—ON THE REDUCTION OF BENZOYL-ORTHO-NITRANILIDE.

By W. G. Mixter.

Hübner[1] obtained by the action of tin and hydrochloric acid on benzoyl-o-nitranilide, benzenylphenylenamidine, $C_{13}H_{10}N_2$. Other reduction products of this ortho-nitranilide do not appear to have been made. It has been shown[2] that para and meta nitranilides yield, when treated with zinc and ammonia, azo and amide bodies, and the following results show the formation of analogous ortho compounds.

Ortho-azoxybenzanilide.

Pure benzoyl-o-nitranilide, prepared from pure o-nitraniline and benzoylchloride, was dissolved in alcohol and pulverised zinc, ammonia and platinic chloride were added. There slowly separated from the solution a yellow fibrous mass, which was filtered off, washed with alcohol, dilute acid, and lastly with water. It was dried at 100° C. The analyses given are of two different preparations.

I. 0.3007 gram yielded 0.7867 gram of CO_2 and 0.1265 gram of H_2O. 0.3175 gram yielded 36.1 cc. of N at 21° C. and 766 mm. pressure.

II. 0.344 gram yielded 0.9098 gram of CO_2 and 0.1466 gram of water. 0.3075 gram yielded 33.9 cc. of N at 19.6° C. and 760 mm. pressure.

	Calculated for $C_{26}H_{20}N_4O_3$.	I.	II.
C	71.56	71.35	72.12
H	4.58	4.67	4.73
N	12.85	13.36	12.93

The ortho-azoxybenzanilide, $\begin{matrix} C_6H_4NHC_7H_5ON \\ | \\ C_6H_4NHC_7H_5ON \end{matrix}\!\!\searrow\!\!\nearrow O$, has a bright yellow color, is insoluble in water and sparingly soluble in boiling alcohol, and melts at 195° C. Attempts were made to remove the benzoyl group by potassium hydroxide and by sulphuric acid, but ortho-azoxyaniline was not obtained.

[1] Annalen der Chemie, **208**, 302.

[2] This Journal, **5**, 1, p. 282.

Benzoyl-ortho-phenylenediamine.

The alcoholic ammonia solution filtered from the azoxybenzanilide was evaporated to dryness, and the residue was digested with a large quantity of boiling water. The clear aqueous solution on cooling yielded minute crystals which melted at 140° C., and gave the following analytical results:

0.2545 gram yielded 0.676 gram of CO_2 and 0.128 gram of H_2O.

0.1447 gram yielded 16.55 cc. of N at 18.6° C. and 757.7 mm. pressure.

	Calculated for $C_6H_4NHC_7H_5ONH_2$.	Found.
C	73.58	72.44
H	5.66	5.59
N	13.30	13.19

The substance appears to be a benzoylphenylenediamine, of which the para and meta modifications are known. The ortho modification, so far as the writer is aware, has not been described. In order to obtain a more satisfactory quantity of this body for analysis, and also for comparison, an attempt was made to prepare it by reducing benzoyl-o-nitranilide with alcoholic ammonium sulphide. The solution, after standing a day, was evaporated to dryness, and the residue was digested with hydrochloric acid. The base was precipitated from the acid solution by ammonia, washed and dried at 100° C.

I. 0.3145 gram yielded 0.8483 gram of CO_2 and 0.1588 gram of H_2O.

II. 0.3294 gram yielded 0.8873 gram of CO_2 and 0.1643 gram of H_2O.

III. 0.1508 gram yielded 17.42 cc. of N at 19° C. and 760 mm. pressure.

	Theory.	I.	II.	III.
C_{13}	73.58	73.56	73.46	
H_{12}	5.66	5.61	5.56	
N_2	13.30			13.56
O	7.46			

The substance is nearly white, is freely soluble in alcohol, and melts at 140° C. It dissolves in warm oil of vitriol, and the solution gives off benzoic acid slowly. Platinic chloride precipitates a slimy salt in an aqueous solution of the hydrochloride. 21.89 per cent. of platinum was found in the salt, which was dried at 100° C.; theory

requires 23.77 per cent. of platinum in $C_6H_4NHC_7H_5ONH_2H_2PtCl_6$. 21.73 per cent. of platinum was found in the platinum salt of the benzoyl-o-phenylenediamine obtained in the reduction with zinc and ammonia. The platinum salt is very soluble in alcohol and tolerably soluble in water. A complete analysis of the platinum salt was impossible, owing to lack of substance.

The mother-liquor from the crystals of benzoyl-phenylenediamine obtained in the reduction by zinc was evaporated, and the residue was dissolved in hydrochloric acid. The base was precipitated by ammonia and analysed with the following results:

	Calculated for $C_{13}H_{10}N_2$.	Found.
C	80.41	77.92
H,	5.16	5.13
N	14.43	14.58
	100	97.63

The analysis shows that nearly all the oxygen had been removed from part of the benzoyl-nitranilide, and indicates the possible formation of benzenylphenylenamidine, $C_{13}H_{10}N_2$. It may be mentioned that no azobenzanilide was obtained.

HEPTANE FROM PINUS SABINIANA.[1]

By C. Schorlemmer and T. E. Thorpe.

In the last communication made by one of us on this subject[2] it was stated that we contemplated making a joint investigation on the heptane from *Pinus Sabiniana*. A large quantity of the pure heptane was treated with chlorine in the manner described in this series of communications,[3] and the chlorides boiling between 143° and 157.5° were converted into the alcohols in the ordinary way. The primary alcohol boiled between 165°–170°,

[1] Communicated by the Authors from the Philosophical Transactions of the Royal Society, Part I, 1883.

[2] Philosophical Transactions, 1880, p. 451.

[3] Philosophical Transactions, 1872, p. 111; and this Journal, **1**, 155.

whilst the secondary alcohol distilled over, for the most part, between 156°–158°. The alcohols were then oxidised in the manner described in the Philosophical Transactions, 1872, p. 121. The ketone obtained from the secondary alcohol was further oxidised by being heated with the chromic acid solution in sealed tubes at 100°. The liquid was then neutralised and the unattacked ketone was separated by distillation. In order to isolate the acids contained in the residue, small quantities of sulphuric acid were added, and the acid which separated out (pentoic acid) was distilled off in a current of steam—the operation being repeated until the pentoic acid was no longer recognisable by its smell. The acetic acid contained in the residue was then separated by a further addition of sulphuric acid and distilled off by direct heating. The respective silver salts of the two acids were then prepared from the several fractions in the ordinary way. Analysis showed that the separation of the acids was complete.

I. Silver salt from the normal alcohol.

(*a*) 0.4035 gram salt gave 0.1842 gram Ag = 45.6 per cent.

(*b*) 0.210 " " 0.0953 " = 45.4 "

Calculated for silver heptoate 45.5 per cent.

II. Silver salts from ketone from secondary alcohol.

0.2022 gram salt A gave 0.1050 gram Ag = 51.9 per cent.

0.1491 " " 0.0771 " = 51.7 "

Silver pentoate = 51.6 Ag.

0.235 gram salt B gave 0.1518 gram Ag = 64.59 per cent.

Silver acetate = 64.67 per cent.

The results of the oxidation show therefore that primary heptyl alcohol and methyl-pentyl-carbinol had been formed, as in the case of heptane from petroleum.

Another portion of the mixture of the monochlorides was then heated to 100° with alcoholic solution of potash, whereby in addition to heptylene a mixture of the ethyl heptyl ethers was obtained. The heptylene, purified by repeated rectification over sodium, boiled constantly at 98.5°. It was placed in contact with an excess of fuming hydrochloric acid in the dark and in a well-closed bottle for six weeks. Heptylene from petroleum heptane was similarly treated.

Now it is remarkable that whilst hexylene from mannite combines completely with hydrochloric acid under these circumstances forming secondary hexyl chloride,[1] the greater part of the heptylene

[1] Philosophical Transactions, 1880, p. 457.

from *Pinus* heptane was found to be unattacked, not more than 10 per cent. of heptyl chloride having been formed. On the other hand, about one-half of the heptylene from petroleum had been converted into the chloride in accordance with the former observations made by one of us on this point.

The uncombined portions of both specimens of heptylene were again placed in contact with the fuming acid, and (the research being interrupted by other work) they were allowed so to remain for many months. At the expiration of this time it was found that the *Pinus* heptylene had united almost completely with the acid, whilst an additional quantity of the heptylene from petroleum had likewise entered into combination. It follows from this that, contrary to expectation, hydrochloric acid acting in the cold is not capable of effecting the separation of isomeric paraffins.[1]

It is remarkable that the *Pinus* heptylene should require so long a time to bring about its union with hydrochloric acid, since, as will be shown immediately, its constitution is exactly analogous to that of the hexylene from mannite or propyl-methyl ethylene, $C_3H_7.CH=CH.CH_3$, which so easily goes into combination.

In order to establish the constitution of the heptylene from *Pinus* it was oxidised by means of a solution of potassium dichromate in dilute sulphuric acid in the manner adopted by Hecht in the oxidation of hexylene from mannite.[2] The acids so formed were converted into the silver salts and analysed with the following results:

Fraction.	Salt taken.	Silver found.	Silver pentoate 51.67.
1	0.0855	0.0443	51.81
2	0.0560	0.02875	51.34
3	0.1140	0.0590	51.75
4	0.1350	0.0700	51.84
5	0.0685	0.0350	51.09
6	0.1000	0.0540	54.00
7	0.2200	0.1370	62.27
8	0.1370	0.0855	64.60
9	0.1400	0.0910	65.00

Silver acetate 64.67.

The first five fractions consisted of a fine crystalline powder, the last three were glistening needles.

These observations clearly indicate that only pentoic and acetic acids had been formed by the oxidation, and therefore that

[1] Philosophical Transactions, 1880, p. 451.

[2] Berichte der deutschen chemischen Gesellschaft, **11**, 1152.

the *Pinus* heptylene is pure butyl-methyl-ethylene, $C_4H_9.CH = CH.CH_3$, which had been formed from the secondary heptyl chloride, $C_4H_9—CH_2—CHCl.CH_3$.

The results, taken in conjunction with those of former investigations, leave no doubt, therefore, that by the action of chlorine upon a normal paraffin, not all the chlorides indicated by theory are formed, but only the primary and a secondary chloride which contains the group $—CHCl.CH_3$. One of us has formerly shown that by the action of bromine upon normal paraffins from petroleum only secondary bromides corresponding to chlorides are formed.[1] Venable has since shown that *Pinus* heptane is acted upon in the same way.[2]

ON SOME NEW FORMS OF ALBUMOSE.[3]

By W. Kühne and R. H. Chittenden.

At the end of our recent paper "on the primary cleavage products of the albumins,"[4] we mentioned the possibility of hemialbumose being a mixture. This idea was suggested to us, first, by the circumstance that all the specimens of hemialbumose which we had prepared yielded by the action of peptone-free trypsin, more or less peptone together with the amido-acids; and, secondly, by certain differences in the solubility of the albumose of different preparations. If the first of these considerations could be overlooked, the second, which we have called particular attention to by the terms "soluble" and "insoluble" hemialbumose, might likewise be considered of little importance, especially when it is remembered that the question as to whether the albumins are really bodies soluble in water has not yet been satisfactorily answered. And as it is often questioned whether the apparent solubility of the albuminous bodies does not depend upon the presence and action of non-removable salts, or of combined acids

[1] Philosophical Transactions, 1878, Part I, p. 49.

[2] Berichte der deutschen chemischen Gesellschaft, **13**, 1649.

[3] An abstract of this paper was read before the National Academy of Sciences, in November, 1883.

[4] Zeitschrift für Biologie, **19**, 159.

or alkalies, so in a similar manner the solubility of hemialbumose might under certain circumstances be considered only as apparent. We have therefore hitherto overlooked this point, and confined ourselves in the preparation and selection of products for study to the following reactions which we deemed characteristic of hemialbumose: 1. In distinction from the albumins: (*a*) solubility in boiling water, in boiling dilute salt solutions even when slightly acidified, with eventual reprecipitation as the solution cools; (*b*) unaltered solubility after precipitation with strong alcohol. 2. In distinction from peptones: (*a*) very slow or imperfect dialysis; (*b*) precipitation by sodium chloride or by sodium chloride and acetic acid, or coagulation at temperatures far below 70° C., with or without the addition of salt and acid, together with solution of the coagulum at temperatures above 70° C. and by boiling. 3. In distinction from the bodies belonging to the anti-group of albumins: decomposition by trypsin with formation of leucin, tyrosin and a body colored violet by bromine. The analyses of hemialbumose showed a content of carbon not over 52.29 per cent. and not under 49.82 per cent.; with an average for hemialbumose from fibrin, the products of which alone will be considered in the present article, of carbon 50.32 per cent.

We had obtained hemialbumose characterised in this manner from coagulated egg-albumin, from the albuminous matter of serum and from fibrin, in part by boiling with diluted sulphuric acid and in part by pepsin digestion; a similar albumose was likewise found present in the urine of a person with osteomalachia. In the preparation of the albumose, one portion of "soluble" albumose was generally obtained, which together with the peptones was dissolved from the alcohol precipitate by cold water; and, secondly, an "insoluble" portion, which was entirely freed from peptones by washing with cold water. The soluble portion was then separated from peptone by boiling with an excess of sodium chloride and some acetic acid. The insoluble portion was purified by solution in boiling water, reprecipitation in the cold, eventually with the aid of alcohol.

In addition to the differences of solubility we noticed later the occurrence of an inconstancy in the reactions, viz. with reference to precipitation of the albumose by sodium chloride; and this led to the method of separation about to be discussed, by which *four* different forms of albumose were isolated from the filtrate

obtained from the neutralisation precipitate in the digestion of fibrin. These are:

No. I. Precipitated by excess of sodium chloride in substance, soluble in cold and hot water.

No. II. Precipitated by excess of sodium chloride, insoluble in cold and in boiling water; but, on the other hand, soluble both in dilute and strong solutions of sodium chloride.

No. III. Similar to No. II, but insoluble in solutions of sodium chloride.

No. IV. Not precipitated by excess of sodium chloride, but precipitated by sodium chloride and acids; soluble in pure water.

On these specific grounds we name No. I. *Protalbumose;* No. IV. *Deuteroalbumose;* No. II. *Heteroalbumose;* No. III. *Dysalbumose;* the "*hemi*" being retained in each case.

These bodies were obtained in part by digestion of fibrin with pepsin-hydrochloric acid, or from the commercial "pepton" manufactured by Witte, and in part from preserved hemialbumose from the urine of a patient with osteomalachia.

Preparation of the different forms of albumose by pepsin digestion.

1500 grams of raw fibrin were placed in 5 litres of 0.4 per cent. hydrochloric acid for twenty-four hours. The swollen mass was then warmed to 45° C., after which 400 cc. of normal gastric juice[1] were added, and the mixture kept at the same temperature for one hour with frequent stirring. After filtering through a hair sieve to remove the small residue of fibrin, the turbid fluid was brought to the faintest possible alkaline reaction with sodium hydroxide and then filtered from the abundant neutralisation precipitate. The clear filtrate was rubbed up with a quantity of sodium chloride, sufficient to insure a slight excess of salt in the abundant white precipitate. The precipitate was washed first upon the filter, with some saturated solution of sodium chloride, then removed from the filter and washed in the most thorough manner possible by trituration with the salt solution. This precipitate contained prot-, dys- and heteroalbumose. From the united filtrates saturated with sodium chloride, deuteroalbumose separated out on the addition of a suitable quantity of 30 per cent. acetic acid in which sodium chloride had been previously dissolved. This precipitate

[1] Compare Zeitschrift für Biologie, **19**, 184.

was less easily collected upon a filter owing to its tendency to form a resinous gum. In the filtrate only traces of albumose were found when the proper quantity of acetic acid had been added; in case the fluid had not been sufficiently acidified, separation of the remaining albumose was accomplished by the addition of more acid, or in case too much acid had been added the excess was easily removed by partial neutralisation. When a good separation had been made there was usually, however, sufficient albumose in the filtrate to yield a turbidity with a little nitric acid, or after boiling the solution, in which case no coagulation was observed, the concentrated solution freed from the deposited salt yielded a small quantity of deuteroalbumose on the addition of a fresh quantity of acetic acid. After this precipitation nothing was found in the residue other than a small quantity of peptone.

The first precipitate produced by sodium chloride alone and freed as completely as possible from the salt solution by pressure was not wholly soluble in water, and its insolubility increased the larger the quantity of water employed. But as it was also not completely soluble in sodium chloride solution of from 1 to 10 per cent., we concluded that this precipitate contained besides a body soluble in water, a second body soluble only in salt solution, and also a third, soluble in neither water nor sodium chloride. The latter (dysalbumose) was obtained as an insoluble residue by simple filtration, trituration and washing first with 5 per cent. sodium chloride solution, and finally with water. The second (heteroalbumose) separated as an insoluble gummy mass by dialysing the salt solution until the chlorine had entirely disappeared, while the first (protalbumose) remained alone in the solution.

In testing the protalbumose for the presence of any traces of the other three bodies, which was accomplished by a repetition of the whole process applied to the dialysed and filtered fluid freed from heteroalbumose, or to the substance precipitated by alcohol, it was found that both hetero- and dysalbumose were absent, but that deuteroalbumose was present to the extent of nearly 50 per cent. For when the solution of whatever concentration was carefully saturated with sodium chloride, a portion only of the substance separated out, while the residue was precipitated only upon the addition of acetic acid.

The latter portion, however, did not consist of deuteroalbumose as would at first appear, for after dialysis or neutralisation of the acetic

acid, it was then found precipitable by sodium chloride, although only partially so, a portion still remaining precipitable only on the addition of acid; the same process continually repeated with this latter portion until the material was entirely used up always led to the same result. The portion precipitated by sodium chloride alone also behaved in the same peculiar manner, being only partially separated from its solution on the second, third and fourth times, etc., by excess of sodium chloride, a portion of what appeared to be deuteroalbumose remaining dissolved each time, and not differing in its properties from that obtained in the first series of experiments.

The first view which quite naturally suggested itself here, viz. that protalbumose by the method of treatment passes over into deuteroalbumose and *vice versa*, is untenable, since we found the latter body prepared by a somewhat different process from different material, not at all precipitable by excess of sodium chloride alone. Deuteroalbumose, therefore, remains characterised by its exclusive precipitation with salt and acid, while to protalbumose is to be ascribed the peculiarity of being only partially precipitated by sodium chloride, a residue remaining each time which requires the presence of acid for its separation.

The further properties of the four varieties of albumose we have studied in the above preparations, prepared from fibrin by pepsin-hydrochloric acid, and later from such preparations as were obtained from commercial material. As, however, no difference was found in the two series of preparations, the following detailed description will answer for the products in each case.

Preparation of the four kinds of albumose from Witte's so-called peptone.

The commercial preparation manufactured in Rostock by Fr. Witte might be made to render great service to the chemistry of digestion, and to this end the unfortunately quite erroneous name of the product needs to be changed to one more strictly descriptive of its nature. The preparation, as is well known to many, contains hardly any peptone, and so long as it is known by that name in the trade this fact cannot but reflect against it. In every other respect we feel compelled to acknowledge our indebtedness to the preparation, in the use of which we had no hesitation, since the

manufacturer of his own accord and in the most friendly manner confided to one of us the secret of the method of preparation. We have found it to contain nothing other than the products naturally to be expected in the immediate solution of well-washed raw fibrin in pepsin digestive mixture, and have found it much preferable to the large quantities of fluid necessarily obtained, and by which our work had hitherto been impeded.[1]

500 grams of the light, white powder were rubbed up with 1500 grams of sodium chloride, whereby the dust immediately disappeared, as the mass became somewhat moist and gummy. To this we added, with vigorous stirring and trituration, 5 litres of water, after which a large piece of rock salt was so placed that it lay on the surface of the mixture. On the next day all that had separated was collected upon a cloth filter and placed under a press. The coarse, almost dry powder was then rubbed up with a large quantity of saturated salt solution, washed and again pressed. Although only slightly moist, the mass weighed almost 500 grams; it was placed in 6 litres of water, after 24 hours clarified by filtration through cloth, precipitated a second time with sodium chloride, of which 1800 grams were added in order to accomplish the saturation. This precipitate, again washed with saturated salt solution and pressed, dissolved almost completely in 2 litres of water, as did also the substance precipitated a third time with sodium chloride. The solution finally obtained was distributed in a large number of dialysing tubes and dialysed in running water until no chlorine reaction could be obtained. In order to prevent precipitation of the albumose in the latter reaction, either by nitric acid alone, or as a silver precipitate, it is necessary to add an excess of nitric acid, or else acetic acid, both to the albumose and silver solution.

During the dialysis numerous lumps of heteroalbumose separated in the tubes, and a gummy layer of the same body was smeared over the entire inner surface of the parchment, which latter could be obtained only by cutting open the tube and scraping it with a spatula.

I. *Protalbumose.*

From the clear aqueous solution, which like all albuminous solutions reacted noticeably alkaline, protalbumose was separated

[1] Witte's "pepton" was likewise recommended for the same purpose by Salkowski, who had recognised the preparation as a mixture of hemialbumose and peptone. Compare Salkowski and Leube, die Lehre vom Harn, 1882, 211.

for the fourth time by salt, again dissolved in water, whereby nothing remained undissolved other than a small amount of gypsum coming from the rock salt, and dialysed, this time with no sign of a turbidity.

During purification the quantity continually and rapidly diminished in favor of a portion always precipitable from the salt saturated filtrate by acetic acid. So in a like manner the final purified product, four times precipitated, was only partially, about half, precipitable by sodium chloride alone. Trituration of the dry substance with solid sodium chloride and then pouring on saturated salt solution likewise failed to produce a complete precipitation, even with a great increase of the absolute quantity of sodium chloride. This latter point is worthy of notice, since frequently a precipitation is obtained in the clear filtrate by the addition of a saturated salt solution alone, in cases where, in spite of the previous saturation of the fluid, there was not enough salt present in proportion to the organic substance. However, none of the substance precipitable by acetic acid from the filtrates of the second to the fourth sodium chloride precipitates agreed with deuteroalbumose, since the solution of each of these precipitates produced after acidifying, were again precipitated by sodium chloride alone, although as before only partially.

Protalbumose was precipitated from the aqueous solution either directly with alcohol, or to economise the alcohol, after concentration. At first fearing alteration of the substance by heat, we carried on the evaporation of the solution at 40° C. (naturally with addition of thymol); but as it soon became apparent that no visible change took place even by boiling, the solutions were finally concentrated on the water-bath.

After precipitation with alcohol, washing with absolute alcohol and finally with ether, protalbumose dries quickly to a snow-white mass, even when in large lumps. It does not dissolve very rapidly in water, but still so abundantly that it is possible to obtain even syrupy solutions. The solutions are colorless, not quite clear, although nearly transparent, and always very slightly alkaline; in which connection it is worth noticing that Witte's preparation reacted faintly acid, and when dissolved in water with a trace of alkali was a little turbid.[1] Exact neutralisation of the

[1] Portions obtained from the manufacturer later were in several cases faintly alkaline.

protalbumose did not change the appearance or behavior of the solution.

The aqueous solution does not become clear at once on the addition of acid, but does finally in the presence of a certain excess of acetic acid; boiling does not affect it even in the presence of a small or great excess of acid; made slightly acid it is not rendered turbid by a little sodium chloride; on the addition of more salt it becomes opalescent, which passes away on the slightest warming, returns by cooling, even when the solution was previously boiled. If sufficient sodium chloride is added to produce in the cold a moderate precipitate, it is at once dissolved to a clear solution by boiling, but reappears as the solution cools. Finally, it is possible to add an amount of sodium chloride in the presence of which the acidified solution will no longer become clear by boiling.

Addition of a few drops of pure nitric acid to a solution of protalbumose free from salt produces a white precipitate, which on shaking is completely redissolved and then is reprecipitated by each new drop of acid added. In this manner it is possible to reach a point when after agitating the solution only a slight turbidity remains, which disappears by warming the solution very gently and again returns on cooling. This relatively small amount of acid is sufficient to produce a faint red (not yellow) color. More nitric acid dissolves the precipitate in the cold with formation of a yellow color; only sodium chloride will produce a precipitate now; the precipitate, however, is completely dissolved by heat, but reappears on cooling.

An aqueous solution of protalbumose strongly acidified with acetic acid is rendered quite turbid by a little potassium ferrocyanide, the precipitate not being dissolved when heated. If the quantity of acetic acid is increased a much larger amount of potassium ferrocyanide is needed to produce a precipitate. It is possible, however, to have the proportion of acid and ferrocyanide such that the mixture appears quite turbid in the cold, but when boiled becomes quite clear, growing turbid again as the solution cools. We have also repeatedly noticed in studying these different forms of albumose, that when mixed in certain proportions the potassium ferrocyanide precipitates are dissolved by a little acetic acid in the cold. These reactions are, however, somewhat uncertain, as the mixtures sooner or later become green or blue from decomposition of the salt.

Sodium hydroxide renders solutions of protalbumose quite clear at first, but when present in excess it causes a turbidity and even produces a precipitate. Solutions which have stood for some time with sodium hydroxide or with dilute hydrochloric acid, or which have been boiled with acetic acid, are not precipitated by neutralisation.

Solution of the substance, saturated with sodium chloride and filtered, is rendered only slightly turbid by boiling and does not become more so when cold. The smallest quantity of acetic acid then produces a heavy turbidity, even at 100° C. Excess of glacial acetic acid renders the fluid perfectly clear, which on being cooled after boiling deposits only crystals of salt. Nitric acid produces the same appearances in the fluid saturated with salt as in solutions free from salt (!).

Of the metallic salts, cupric sulphate, mercuric chloride and basic lead acetate produce heavy precipitates; the first and last, in contradistinction to the mercuric chloride precipitate, being soluble in excess of the reagent; all three of the precipitates, however, appear not to be even partially soluble on heating. Neutral lead acetate added to a faintly acid solution of protalbumose fails to produce any precipitate whatever, but the first few drops added to a really alkaline solution produce a precipitate which, however, is redissolved by an excess of lead.

With sodium hydroxide and a little dilute cupric sulphate a beautiful reddish violet color is produced. By boiling with lead acetate and an alkali hydroxide a deep blackening of the solution occurs, from the formation of lead sulphide.

We found the same reactions to be good also for that portion of the protalbumose not precipitated by sodium chloride alone. This portion was prepared by adding acetic acid to the filtrate saturated with salt, dissolving the precipitate in water, neutralising, dialysing, evaporating at 40° C., and finally precipitating with alcohol. Both portions of protalbumose were found to be not completely precipitated by trituration with excess of magnesium sulphate nor by saturation with sodium sulphate and sodium chloride, as the filtrates in each case saturated with the salts were still precipitated by acetic acid.

In determining the composition of protalbumose five different preparations were employed:

A, purified by being four times precipitated;

B, purified by three precipitations;

C, prepared directly from an artificial digestion of fibrin, purified by two precipitations;

D, prepared from the same material as *C*, being the first portion precipitated by sodium chloride alone;

E, obtained in the same manner as *C* and *D*, being the second portion, precipitated by acetic acid after saturation with salt.

With the exception of *A*, which contained a trace of chlorine, all of the preparations were found, when tested both in concentrated solutions and after ignition, to be entirely free from chlorine. The content of ash was variable, in some cases being very small, and depended exclusively or at least in great part on the amount of calcium sulphate contained in the rock salt; after making the sulphur determinations the sulphur of the ash was deducted. Carbonate was present in the ash only once and then only in traces. The method of analysis was similar to that employed previously;[1] the substance in the form of a fine powder was dried at 105° C. *in vacuo*, carbon and hydrogen were determined by burning with cupric oxide, lead chromate and a roll of metallic copper in oxygen gas, nitrogen was determined as gas by burning with cupric oxide and a layer of metallic copper in a tube exhausted by a Sprengel pump, the sulphur by fusion with potassium hydroxide and nitrate and precipitation as barium sulphate.

A.

I. 0.4864 gram gave 0.2985 gram H_2O = 6.81 per cent. H and 0.9009 gram CO_2 = 50.50 per cent. C.

II. 0.4594 gram gave 0.2790 gram H_2O = 6.75 per cent. H and 0.8487 gram CO_2 = 50.38 per cent. C.

III. 0.6136 gram gave 89.63 cc. N at 23° C. and 760.45 mm. pressure = 0.1038901 gram N = 16.93 per cent.

IV. 0.4430 gram gave 63.96 cc. N at 21.6° C. and 766.5 mm. pressure = 0.0750823 gram N = 16.94 per cent.

V. 0.4720 gram gave 68.76 cc. N at 22.8° C. and 767 mm. pressure = 0.0804362 gram N = 17.04 per cent.

VI. 0.6234 gram gave 0.0055 gram ash = 0.89 per cent.

VII. 0.5206 gram gave 0.0048 gram ash = 0.92 per cent.

The ash consisted mainly of calcium sulphate and was free from carbonate; the ash from 1.1440 grams substance dissolved in dilute

[1] Compare Zeitschrift für Biologie, **19**, 166.

hydrochloric acid gave with $BaCl_2$ 0.0111 gram $BaSO_4$ = 0.10 per cent. S, calculated on the original substance.

VIII. 0.5289 gram substance gave, after fusion with potassium hydroxide and nitrate, 0.0472 gram $BaSO_4$ = 1.22 per cent. S; deducting 0.10 per cent. as coming from the ash = 1.12 per cent. S.

IX. 0.5130 gram gave, after the fusion, 0.0483 gram $BaSO_4$ = 1.29 per cent. S; deducting 0.10 per cent. = 1.19 per cent. S.

Percentage composition of ash-free protalbumose *A*:

								Average.
C	50.95	50.83	...	...	...	...	...	50.89
H	6.87	6.80	...	...	...	...	...	6.83
N	...	..	17.08	17.09	17.18	...	...	17.12
S	...	...	...	...	...	1.14	1.20	1.17
O	...	...	...	...	...	...	...	23.99

B.

I. 0.5466 gram gave 0.3335 gram H_2O = 6.77 per cent. H and 1.0070 grams CO_2 = 50.23 per cent. C.

II. 0.5785 gram gave 0.3485 gram H_2O = 6.69 per cent. H and 1.0656 grams CO_2 = 50.23 per cent. C.

III. 0.5731 gram gave 0.3470 gram H_2O = 6.72 per cent. H and 1.0587 grams CO_2 = 50.37 per cent. C.

IV. 0.5698 gram gave 83.11 cc. N at 20.6° C. and 766.08 mm. pressure = 0.0978412 gram N = 17.17 per cent.

V. 0.7647 gram gave 111.38 cc. N at 20.6° C. and 759.38 mm. pressure = 0.1299753 gram N = 17.00 per cent.

VI. 0.8427 gram gave 0.0018 gram ash = 0.21 per cent.

VII. 0.6890 gram gave 0.0016 gram ash = 0.23 per cent.

The ash contained no carbonate, only calcium sulphate; the ash from 1.5317 grams substance gave 0.0037 gram $BaSO_4$ = 0.03 per cent. S.

VIII. 0.6925 gram substance gave after fusion with potassium nitrate 0.0538 gram $BaSO_4$ = 1.06 per cent. S; after deducting the 0.03 per cent. S from the ash = 1.03 per cent. S.

IX. 0.6170 gram gave 0.0521 gram $BaSO_4$ = 1.15 per cent. S; deducting 0.03 per cent. = 1.12 per cent. S.

Percentage composition of ash-free protalbumose *B*:

								Average.
C	50.35	50.35	50.48	...	...	...	...	50.39
H	6.78	6.70	6.73	...	...	...	...	6.74
N	...	...	...	17.20	17.04	...	...	17.12
S	...	...	...	...	...	1.03	1.12	1.07
O	...	...	...	...	...	...	...	24.68

C.

I. 0.7103 gram gave 0.4176 gram H_2O = 6.53 per cent. H and 1.2808 grams CO_2 = 49.17 per cent. C.

II. 0.6136 gram gave 0.3600 gram H_2O = 6.51 per cent. H and 1.1097 grams CO_2 = 49.31 per cent. C.

III. 0.3551 gram gave 0.2088 gram H_2O = 6.53 per cent. H and 0.6411 gram CO_2 = 49.23 per cent. C.

IV. 0.6507 gram gave 94.38 cc. N at 20° C. and 757.33 mm. pressure = 0.1100642 gram N = 16.91 per cent.

V. 0.5481 gram gave 78.82 cc. N at 19.2° C. and 761.45 mm. pressure = 0.0926730 gram N = 16.90 per cent.

VI. 0.5407 gram gave 0.0138 gram ash = 2.55 per cent.

VII. 0.6306 gram gave 0.0165 gram ash = 2.61 per cent.

The ash was composed of calcium sulphate, with a trace of calcium phosphate without any carbonate.

The ash from 1.1713 grams substance gave 0.0427 gram $BaSO_4$ = 0.50 per cent. S contained in the ash of the original substance.

VIII. 0.6163 gram gave after fusion with the nitrate 0.0705 gram $BaSO_4$ = 1.57 per cent. S; deducting 0.50 per cent. as coming from the ash = 1.07 per cent. S.

IX. 0.5373 gram gave 0.0664 gram $BaSO_4$ = 1.69 per cent. S; deducting 0.50 per cent. = 1.19 per cent. S.

Percentage composition of ash-free protalbumose *C*:

								Average.
C	50.47	50.62	50.53	...	...	...	...	50.54
H	6.70	6.68	6.70	...	...	...	...	6.69
N	...	...	...	17.35	17.34	...	...	17.34
S	...	...	...	...	...	1.11	1.23	1.17
O	...	...	...	...	...	...	...	24.26

D.

I. 0.6067 gram gave 0.3686 gram H_2O = 6.75 per cent. H and 1.1323 grams CO_2 = 50.89 per cent. C.

II. 0.5643 gram gave 0.3403 gram H_2O = 6.70 per cent. H and 1.0567 grams CO_2 = 51.06 per cent C.

III. 0.6055 gram gave 0.3676 gram H_2O = 6.74 per cent. H and 1.1315 grams CO_2 = 50.95 per cent. C.

IV. 0.6757 gram gave 97.98 cc. N at 19.8° C. and 760.38 mm. pressure = 0.1148016 gram N = 16.98 per cent.

V. 0.6348 gram gave 90.28 cc. N at 18.3° C. and 768.66 mm. pressure = 0.1074839 gram N = 16.93 per cent.

VI. 0.6609 gram gave 0.0070 gram ash = 1.05 per cent.

VII. 1.1512 grams gave 0.0124 gram ash = 1.07 per cent.

The ash contained no carbonate, only calcium sulphate.

The ash from 1.8121 grams substance gave 0.0175 gram $BaSO_4$ = 0.13 per cent. S, calculated on the original substance.

VIII. 0.6650 gram gave after the nitrate fusion 0.0525 gram $BaSO_4$ = 1.08 per cent. S; deducting the 0.13 per cent. S of the ash = 0.95 per cent.

IX. 0.5643 gram gave 0.0425 gram $BaSO_4$ = 1.03 per cent. S; deducting 0.13 per cent. = 0.90 per cent. S.

Percentage composition of the ash-free protalbumose *D*:

								Average.
C	51.43	51.60	51.49	...	...	...	...	51.50
H	6.82	6.77	6.81	...	...	...	...	6.80
N	...	...	...	17.16	17.11	...	...	17.13
S	...	...	...	...	...	0.96	0.91	0.94
O	...	...	...	...	...	...	...	23.63

E.

I. 0.3993 gram gave 0.2445 gram H_2O = 6.80 per cent. H and 0.7329 gram CO_2 = 50.05 per cent. C.

II. 0.5722 gram gave 0.3452 gram H_2O = 6.70 per cent. H and 1.0437 grams CO_2 = 49.74 per cent. C.

III. 0.7986 gram gave 0.4890 gram H_2O = 6.80 per cent. H and 1.4610 grams CO_2 = 49.88 per cent. C.

IV. 0.4635 gram gave 66.16 cc. N at 19.8° C. and 763.4 mm. pressure = 0.0778265 gram N = 16.79 per cent.

V. 0.5845 gram gave 83.56 cc. N at 19.6° C. and 761.26 mm. pressure = 0.0980867 gram N = 16.78 per cent.

VI. 0.8561 gram gave 0.0115 gram ash = 1.34 per cent.

VII. 0.6389 gram gave 0.0083 gram ash = 1.30 per cent.

The ash contained no carbonic acid, only calcium sulphate and a trace of phosphate.

The ash from 1.4950 grams substance gave 0.0091 gram $BaSO_4$ = 0.08 per cent. S, calculated on the original substance.

VIII. 0.5187 gram gave in the nitrate fusion 0.0426 gram $BaSO_4$ = 1.12 per cent. S; deducting 0.08 per cent. as coming from the calcium sulphate of the ash = 1.04 per cent. S.

IX. 0.7779 gram gave by fusion 0.0642 gram $BaSO_4$ = 1.13 per cent. S; deducting 0.08 per cent. = 1.05 per cent. S.

Percentage composition of the ash-free protalbumose *E*:

								Average.
C	50.71	50.40	50.55	...	...	...	...	50.55
H	6.89	6.78	6.89	...	...	...	...	6.85
N	...	...	...	17.01	17.00	...	...	17.01
S	...	...	...	...	...	1.06	1.07	1.07
O	...	...	...	...	...	...	...	24.52

The analyses show such close agreement it is evident that the five preparations cannot be considered as bodies of noticeably different percentage composition. The very slight differences vary on an average in such a manner that, while the nitrogen (the values of which are naturally to be considered as somewhat high) shows hardly any variation, lower percentages of carbon answer to higher percentages of hydrogen, so that the slight differences are without doubt due to small fluctuations in the content of water. In this manner the two products obtained from *C*, viz. *D* and *E*, can be distinguished, the acetic acid precipitate (*E*) being considered as the hydrate.

As special value has of late been laid upon the specific rotary power of the different albumins and their digestive products, an attempt was made to determine these physical characters of the several specimens of protalbumose. Unfortunately we were not able to carry out the observations in as exact a manner as seemed to us desirable, since concentrated solutions were as a rule too turbid for use; and even in the more dilute solutions it was necessary, in making an observation with a tube 200 millimetres long, to clarify the solution with a little hydrochloric acid, which might possibly alter its rotary power, in order to render it sufficiently transparent. The determinations were made by means of a large Wild's polaristrobometer with sodium light. They led to the following results:

Protalbumose A.

0.7986 gram substance dried at 105° C. *in vacuo* = 0.7915 gram ash-free substance dissolved in 40 cc. H_2O + 10 cc. 0.2 per cent. HCl, rotated the plane of light 2.3° to the left as an average of 3 determinations in a 200 mm. tube. Therefore, with 0.015883 gram of pure substance in 1 cc.,

$$(\alpha)_D = \frac{2.3^\circ}{0.015883 \cdot 2} = -72.64^\circ.$$

Protalbumose B.

1.1411 grams dried in the same manner as $A = 1.1386$ gram ash-free substance dissolved in 40 cc. H_2O + 10 cc. 0.2 per cent. HCl rotated the plane of light as a mean of 5 observations 3.6° to the left; thus, with 0.02277 gram pure substance in 1 cc.,

$$(\alpha)_D = \frac{3.6°}{0.02277 \cdot 2} = -79.05°.$$

Protalbumose C.

0.9881 gram dry = 0.9627 gram ash-free substance dissolved in 30 cc. H_2O + 20 cc. 0.2 per cent. HCl; rotation as a mean of 4 observations 3.0° to the left. With 0.019254 gram pure substance in 1 cc.,

$$(\alpha)_D = \frac{3.0°}{0.019254 \cdot 2} = -77.90°.$$

Protalbumose D.

0.6905 gram dry = 0.6832 gram ash-free substance dissolved in 35 cc. H_2O + 15 cc. 0.2 per cent. HCl; rotation as a mean of 3 observations 2.0° to the left. With 0.013664 gram pure substance per cubic centimetre,

$$(\alpha)_D = \frac{2.0°}{0.013664 \cdot 2} = -73.18°.$$

Protalbumose E.

0.8515 gram dry = 0.8403 gram ash-free substance dissolved in 30 cc. H_2O + 20 cc. 0.2 per cent. HCl; rotation as a mean of 4 observations 2.4° to the left. Therefore, with 0.016806 gram pure substance per cubic centimetre,

$$(\alpha)_D = \frac{2.4°}{0.01680 \cdot 2} = -71.40°.$$

The specific rotary power certainly varies in these preparations to a not inconsiderable extent, the maximum variation being 7.65°; we are, however, of the opinion that in order to draw any conclusion from these determinations, more exact studies of the influence of the solvent used in rendering the solutions transparent are necessary.

II. *Deuteroalbumose.*

We have obtained this body in the purest condition from Witte's albumose. The method of separation consisted in the addition of acetic acid to the filtrate (to which the salt solution used in washing the protalbumose had not been added) from the first salt-albumose precipitate. It was an easy matter to collect the precipitate formed in this manner on a cloth filter, and after thorough washing with saturated salt solution the mass was found to be so pure that it needed only one more precipitation with salt and acid. On dialysis the substance parted with the last portions of acid quite slowly; it therefore seemed desirable after the removal of the greater portion of the acid to neutralise carefully with sodium hydroxide, so that at the last only the acetate remained for further dialysis. In no case was a turbidity noticed either on neutralisation or after removal of the acetic acid by dialysis,[1] by which, however, the solution became noticeably alkaline. On the other hand it was occasionally necessary to remove from the neutralised fluid a deposit of hetero-albumose which had separated during dialysis.

From the thoroughly dialysed solution deuteroalbumose was obtained by evaporation, precipitation with alcohol, washing with absolute alcohol and ether, as a white, light powder, which aside from a slight admixture of gypsum (0.68–1.77 per cent.) was apparently quite pure. A solution of the substance could be concentrated on a water-bath without suffering any noticeable change. Following are the general characters of the body.

It is not precipitated by saturation with sodium chloride; after standing days and even weeks with an excess of clean salt crystals the solution remained perfectly clear, and after filtration and washing with saturated salt solution nothing remained upon the filter which would give to suitable solvents anything colored yellow by nitric acid. By boiling the solution saturated with sodium chloride

[1] This removal of the acid by dialysis succeeds with many of the albuminous bodies; a solution of flesh- (myosin-) syntonin, for example, in HCl of from 0.1–0.5 per cent. with or without the addition of thymol is in this manner completely precipitated neutral and free from chlorine; in a similar manner a digestive mixture with pepsin-HCl will deposit not only the whole of the so-called neutralisation precipitate, but also hetero- and dysalbumose. With the various forms of albumose, however, complete removal of the acid by dialysis is less to be recommended, since these bodies though difficultly diffusible, pass through parchment much more rapidly than the original albumin, and thus the loss by long-continued dialysis becomes quite appreciable. On the other hand dialysis is peculiarly adapted to the precipitation of myosin-salt solutions, which as is well known require for their precipitation with water the addition of very large quantities and at the same time give a too finely divided precipitate. In the dialyser, however, the volume of fluid is but little increased, while the precipitate which forms is very compact and does not become difficultly soluble in salt solutions of suitable strength.

no special precipitation is to be seen, but the fluid resembles a frothy jelly filled with bubbles, which appearance disappears on cooling, or at the most in place of the shrunken froth is to be seen only a few short white shreds or fibres.

A solution of deuteroalbumose free from salt, made by dissolving some of the pure substance in cold, distilled water, is not altered by boiling and cooling, not even after acidifying slightly with acetic acid; by nitric acid in any proportion and at any temperature the solution is not rendered turbid, though a slight excess of acid produces a yellow color even in the cold. If the yellow solution is mixed with sufficient sodium chloride to produce a strong turbidity and then warmed, the solution becomes perfectly clear long before the boiling point is reached, but as the solution cools the turbidity reappears. The same reactions appear when a little sodium chloride is added before acidifying. Solution of the albumose made faintly acid with acetic acid and then mixed with a few drops of sodium chloride solution can remain perfectly clear; as the solution is gently warmed a turbidity appears, which by stronger heat entirely passes away, the solution becoming once more clear; then on cooling a permanent turbidity makes its appearance, which, however, can be made to disappear by heating the solution nearly to boiling. On the addition of more sodium chloride a point is reached where the moderate-sized precipitate formed is entirely dissipated by heat, reappearing as the solution cools; and then again there is another proportion where a slight turbidity remains on boiling, and finally still another where an apparently constant precipitate is formed at 100° C. If now the latter mixture is filtered hot, the solution at first passes through the paper perfectly clear, but on cooling a decided turbidity appears. This also happened when solid sodium chloride had been added to saturation, equally as well whether the amount of acid present was small or quite large. In the latter case the clear fluid filtered from the precipitate which formed prior to the heating gives by moderate warming a precipitate which disappears by stronger heat, remaining clear even when the solution becomes cold. If an excess of either ordinary or glacial acetic acid saturated with salt be added to a salt-saturated solution of deuteroalbumose, the precipitate is completely dissolved even in the cold; boiling and then cooling the solution has no effect on it whatever.

Towards acetic acid and potassium ferrocyanide deuteroalbumose behaves in all respects exactly like protalbumose, also towards

neutral and basic lead acetate, cupric sulphate, mercuric chloride, sodium hydroxide and cupric sulphate; boiling with sodium hydroxide and lead acetate produces a deep blackening.

By the long-continued action of sodium hydroxide, of one per cent. hydrochloric acid, and by boiling with acetic acid, deuteroalbumose does not become precipitable by neutralisation.

The analyses were of preparations (*F* and *G*) made by two processes, both obtained from the product manufactured by Witte.

Deuteroalbumose F.

I. 0.5640 gram gave 0.3340 gram H_2O = 6.58 per cent. H and 1.0247 grams CO_2 = 49.54 per cent. C.

II. 0.4595 gram gave 0.2814 gram H_2O = 6.80 per cent. H and 0.8354 gram CO_2 = 49.57 per cent. C.

III. 0.5715 gram gave 0.3452 gram H_2O = 6.71 per cent. H and 1.0400 grams CO_2 = 49.62 per cent. C.

IV. 0.5508 gram gave 78.82 cc. N at 20.8° C. and 766.26 mm. pressure = 0.0927552 gram N = 16.83 per cent.

V. 0.4684 gram gave 67.76 cc. N at 21.3° C. and 766.8 mm. pressure = 0.0796552 gram N = 17.00 per cent.

VI. 0.3262 gram gave 47.08 cc. N at 19.6° C. and 758.4 mm. pressure = 0.0550571 gram N = 16.87 per cent.

VII. 0.6600 gram gave 0.0120 gram ash = 1.81 per cent.

VIII. 0.7260 gram gave 0.0127 gram ash = 1.74 per cent.

The ash contained a trace of carbonate and phosphate, but consisted mainly of calcium sulphate.

The ash from 1.3860 grams substance gave 0.0173 gram $BaSO_4$ = 0.17 per cent S in the original substance.

IX. 0.6845 gram gave after the nitrate fusion 0.0501 gram $BaSO_4$ = 1.00 per cent S; deducting the 0.17 per cent. S present in the gypsum = 0.83 per cent. S.

X. 1.0256 grams gave after the nitrate fusion 0.0770 gram $BaSO_4$ = 1.03 per cent. S; deducting 0.17 per cent. = 0.86 per cent. S.

Percentage composition of ash-free deuteroalbumose *F*:

									Average.
C	50.43	50.46	50.51	...	...	...	...	...	50.47
H	6.69	6.91	6.83	...	...	...	...	...	6.81
N	...	...	...	17.13	17.30	17.17	...	...	17.20
S	...	...	...	...	...	...	0.85	0.88	0.87
O	...	...	...	...	...	...	...	...	24.65

Deuteroalbumose G.

I. 0.4631 gram gave 0.2865 gram H_2O = 6.87 per cent. H and 0.8603 gram CO_2 = 50.66 per cent. C.

II. 0.5730 gram gave 0.3500 gram H_2O = 6.78 per cent. H and 1.0598 grams CO_2 = 50.43 per cent. C.

III. 0.5302 gram gave 0.3228 gram H_2O = 6.76 per cent. H and 0.9800 gram CO_2 = 50.40 per cent. C.

IV. 0.4824 gram gave 70.15 cc. N at 21.2° C. and 765.14 mm. pressure = 0.0823142 gram N = 17.06 per cent.

V. 0.5630 gram gave 81.07 cc. N at 20.6° C. and 766.65 mm. pressure = 0.0955107 gram N = 17.00 per cent.

VI. 0.6434 gram gave 0.0046 gram ash = 0.70 per cent.

VII. 0.7275 gram gave 0.0048 gram ash = 0.66 per cent.

The ash contained no carbonic acid, but consisted wholly of calcium sulphate.

The ash from 1.3709 grams substance gave 0.0059 gram $BaSO_4$ = 0.06 per cent. S, calculated on the original substance.

VIII. 0.7779 gram substance gave by the nitrate fusion 0.0639 gram $BaSO_4$ = 1.12 per cent. S; deducting 0.06 per cent. = 1.06 per cent. S.

IX. 0.5180 gram gave by the nitrate fusion 0.0425 gram $BaSO_4$ = 1.12 per cent. S; deducting 0.06 per cent. = 1.06 per cent. S.

Percentage composition of ash-free deuteroalbumose *G*:

								Average.
C	51.00	50.77	50.75	...	...	...	...	50.84
H	6.92	6.83	6.81	...	...	...	...	6.85
N	...	...	...	17.17	17.11	...	...	17.14
S	...	...	...	...	...	1.07	1.07	1.07
O	...	...	...	...	...	...	...	24.10

Examination of the specific rotary power gave the following results:

Deuteroalbumose *F*: 0.8550 gram dry substance = 0.8399 gram ash-free substance dissolved in 35 cc. H_2O + 15 cc. 0.2 per cent. HCl rotated the light 2.5° to the left, as a mean of 4 observations in a 200 mm. tube, hence with 0.016798 gram pure substance per cubic centimetre,

$$(\alpha)_D = \frac{2.5^\circ}{0.016798 \cdot 2} = -74.41^\circ.$$

Deuteroalbumose *G*: 0.7635 gram dry = 0.7584 gram ash-free substance dissolved in 40 cc. H_2O + 10 cc. 0.2 per cent. HCl

rotated the light as a mean of 4 observations 2.4° to the left; thus with 0.015168 gram pure substance in 1 cc.,

$$(\alpha)_D = \frac{2.4^\circ}{0.015168 \cdot 2} = -79.11^\circ.$$

Deuteroalbumose does not therefore differ essentially either in composition or in its optical properties from protalbumose; both are to be considered on like grounds as the first hydrates of albumin.

(To be continued.)

INVESTIGATIONS ON SINAPINE.

I.—ON SINAPIC ACID.

By Ira Remsen and R. D. Coale.

In the year 1825 Henry and Garot[1] discovered a new substance in white mustard seed, and to it they gave the name *sulphosinapic acid.* In 1852 von Babo and Hirschbrunn[2] published the results of an elaborate investigation of this substance, since which time practically nothing has been added to our knowledge of the subject. What is at present known may be briefly summed up. The substance which can be extracted from mustard seed by alcohol is the sulphocyanate of a base known as sinapine. The base has the composition represented by the formula $C_{16}H_{23}NO_5$, the sulphocyanate being $C_{17}H_{24}N_2SO_5$. When the base is boiled with an alkali it undergoes decomposition, yielding two products, *sinapic acid* and *sincaline*, a new base. The decomposition is represented by the equation:

$$C_{16}H_{23}NO_5 + 2H_2O = \underset{\text{Sincaline.}}{C_5H_{15}NO_2} + \underset{\text{Sinapic Acid.}}{C_{11}H_{12}O_5}.$$

Claus and Keesé[3] have examined sincaline, and have made it appear extremely probable that this base is identical with the substance known as choline, bilineurine and trimethylethoxy-

[1] Journ. Pharm. **17**, 1; **20**, 63.
[2] Annalen der Chemie, **84**, 10.
[3] Zeitschrift für Chemie, 1868, 46.

ammonium hydroxide $(CH_3)_3N(C_2H_5O).OH$. Satisfactory proofs of the identity have, however, not been furnished.

As regards sinapic acid the only facts established by von Babo and Hirschbrunn are the composition, represented by the formula $C_{11}H_{12}O_5$, the instability of its salts and the composition of a barium salt, $C_{11}H_{10}O_5Ba$. After giving the results of the analyses of this salt von Babo says: "Da es nicht leicht ist, ein anderes Salz der Säure in zur Analyse geeignetem Zustand zu erhalten und ich nicht zu viel Material diesen Versuchen opfern konnte, musste die Entscheidung der Frage, ob die Säure ein- oder zweibasisch ist, für jetzt unterbleiben." As the salt was prepared by treating the acid with an excess of baryta water, the fact that it has the composition $C_{11}H_{10}O_5Ba$ might indicate that the acid is bibasic, or that it contains phenol hydroxyls, or, finally, one hydroxyl and one carboxyl. According to the formula above given it has the composition of a propyl ether of one of the hydroxy-phthalic acids, $C_6H_3\begin{cases}OC_3H_7\\(COOH)_2\end{cases} = C_{11}H_{12}O_5$. This fact awakened our interest in the acid, as the researches of one of us during the past few years have had more or less connection with the hydroxy-phthalic acids. We have hence undertaken a new investigation of sinapine and its decomposition products, and in this paper will communicate the results reached in connection with sinapic acid, leaving for a future communication the subject of sincaline. Various circumstances have tended to delay the progress of the investigation, and even now the results are not all that we could wish for. As we have, however, succeeded in throwing considerable light upon the nature of sinapic acid, and have indeed reached a definite conclusion concerning its constitution, we give here the results already obtained, hoping soon to be able to conclude the investigation.

Preparation of Sulphocyanate of Sinapine.

According to von Babo and Hirschbrunn the maximum yield of the sulphocyanate obtainable is 0.5 gram from a pound of white mustard seed. In order to obtain a sufficient quantity to work with satisfactorily, it was hence necessary to start with a large quantity of mustard seed. We had 100 pounds of unground white mustard seed thoroughly pressed, to free it from oil, and then placed the pressed seed in the hands of a manufacturing chemist who kindly undertook for us the work of extraction. This was

accomplished as follows: The seed was digested in portions of 10 pounds each with four to five gallons of 95 per cent. alcohol. About one gallon of the alcohol remained in each portion and could not be recovered by filtration and pressure. The combined alcoholic extracts were evaporated until one gallon of the residue represented 10 pounds of the seed. This concentrated extract was delivered to us and formed the starting point of our work. It was further concentrated by distillation to about one-fifth its volume and divided into four equal portions of two to three litres each. To one of these portions a small quantity of an alcoholic solution of potassium sulphocyanate was added, and after a few days this portion was found to be filled with a mass of feathery crystals, while the other portions were free from the deposit. These were therefore also treated with an alcoholic solution of potassium sulphocyanate, and in a few days the crystals appeared in them as in the first portion. The crystals were filtered off through cotton cloth, pressed carefully and then recrystallised from water. The alcoholic mother-liquors were placed aside, and, after standing for some days, crystals were again deposited from them. From time to time these successive deposits were filtered off, pressed and recrystallised, and were thus easily obtained in pure condition. Two crystallisations from water were usually quite sufficient to thoroughly purify the substance. We obtained in all about 80 grams of the pure substance from 100 pounds of the seed, a somewhat better yield than that obtained by von Babo and Hirschbrunn, which, as stated above, was only 0.5 gram from a pound of mustard seed. These chemists seem to have had much more difficulty in getting the crystals out of their extracts than we had. They recommend that the extracts be distilled until the greater part of the alcohol has passed over, and the residue on cooling separates into two layers about equal in size, one of oil and the other of the solution of sinapine sulphocyanate. They say that the entire success of the operation depends upon hitting exactly the right concentration of the liquid. If the evaporation is not carried far enough a great deal of sinapine remains in the oil. If, on the other hand, the evaporation is carried too far, the sinapine undergoes decomposition, or products are formed which prevent its crystallisation. At first we tried faithfully to hit the proper concentration at which the liquid should separate into two layers. After a great many efforts we finally gave this up, and worked as above described, and with entirely satisfactory results. The use of

a centrifugal machine for the purpose of freeing the crystals from the thick mother-liquor we have also found unnecessary. Athough the first deposit contained indeed some gummy matter, and its filtration was not effected as easily as that of the succeeding portions, still it was easily purified by crystallising from water, in which the gummy matter appeared to be entirely insoluble. The purification by crystallisation from water appears to be much more satisfactory than that from alcohol, as recommended by von Babo and Hirschbrunn.

The sulphocyanate of sinapine obtained as above described crystallises from water in beautiful, feathery crystalline masses. It is nearly colorless, though repeated crystallisations failed to remove a slight yellowish tint. It is difficultly soluble in cold water, easily in hot. It melts at 176°, not at 130° as stated by von Babo and Hirschbrunn. In other respects the properties of our product agree perfectly with those given by these authors.

Preparation of Sinapic Acid from Sinapine Sulphocyanate.

Von Babo and Hirschbrunn effected the decomposition of sinapine into sincaline and sinapic acid by boiling with caustic potash. On then adding hydrochloric acid, the acid was thrown down. In preparing sincaline, however, they used baryta water, thus obtaining the acid in the form of an insoluble, stable barium salt. We have found that for the purpose of preparing the acid the decomposition of the sinapine is best effected by means of baryta water. Our process is as follows: 20 grams barium hydroxide are dissolved in 300 cc. water and 10 grams of the sulphocyanate of sinapine added. The solution turns markedly yellow, and a yellow precipitate is formed. The mixture is boiled for a few minutes to complete the decomposition, and the precipitate then filtered off. It is washed with water, brought into a flask and treated with dilute hydrochloric acid. The sinapic acid is thus obtained in the form of a dirty white precipitate. It is crystallised from water, the quantity obtained in a single experiment being soluble in 500 cc. hot water. From the solution it is deposited in fine well-formed needles which have a slight yellow color. The yield from 10 grams sulphocyanate of sinapine is about 6 grams, the theoretical yield being but a small fraction more than 6 grams. On concentrating the mother-liquor it becomes dark colored, and on cooling deposits a reddish-brown gelatinous mass. This is at least partly

due to a slight decomposition of the acid by boiling with water alone, for the same thing was noticed when the purest acid was dissolved in water and the solution concentrated by boiling. This decomposition appears not to take place to as great an extent by boiling with alcohol or with alcohol and water. We have hence commonly employed a mixture of alcohol and water for the purpose of purifying it. The method finally adopted consisted in dissolving the acid in a small quantity of hot alcohol, then adding water until a precipitate was formed, heating gently until this dissolved, and then allowing to cool. The fusing points of different specimens vary. That which was crystallised from alcohol and water fused at 192° (corrected), and that from alcohol alone at 186.5° (corrected). The discoverers state that it melts "ohngefähr bei 150° bis 200.°"

The acid is difficultly soluble in cold water and cold alcohol, and easily soluble in the hot liquids. The crystals from the alcoholic solution are small transparent prisms, with a yellow color which could not be removed. Those from the aqueous solution are smaller. Both have the appearance of being perfectly homogeneous. As already mentioned, slight decomposition appears to take place more easily in the aqueous than in the alcoholic solutions. To determine whether this decomposition materially affected the composition of the substance, a number of combustions were made of products from various crystallisations. The first two analyses are of crystals obtained from water alone. The next two are of crystals obtained from alcohol and water—no special care being taken in regard to the time of boiling. The substance was dried at 130° before the analyses. The results obtained are here given:

I. 0.2988 gram substance gave 0.6399CO_2; and 0.1787 gram H_2O.

II. 0.2012 gram substance gave 0.4346CO_2; and 0.1124 gram H_2O.

III. 0.1998 gram substance gave 0.4333CO_2; and 0.1090 gram H_2O.

IV. 0.2015 gram substance gave 0.4370CO_2; and 0.1266 gram H_2O.

The substance used in the two next analyses was prepared in the same way as that used in the preceding ones, only, instead of being dried at 130°, it was dried by pressure between layers of bibulous paper and by standing in the air. The results are:

V. 0.2008 gram substance gave 0.4357 gram CO_2; and 0.1085 gram H_2O.

VI. 0.2008 gram substance gave 0.4367 gram CO_2; and 0.1073 gram H_2O.

The same substance was now recrystallised from alcohol and water, and dried in the air at the ordinary temperature. The results are:

VII. 0.2007 gram substance gave 0.4348 gram CO_2; and 0.1053 gram H_2O.

A new quantity of the acid was now prepared, and, in crystallising it, precautions were taken to perform the operation as rapidly as possible so as to reduce the risk of decomposition. It was crystallised from alcohol and water, and dried at 130°. The results of the analyses are:

VIII. 0.2003 gram substance gave 0.4302 gram CO_2; and 0.0921 gram H_2O.

IX. 0.2004 gram substance gave 0.4318 gram CO_2; and 0.1032 gram H_2O.

X. 0.2009 gram substance gave 0.4320 gram CO_2; and 0.1006 gram H_2O.

XI. 0.2495 gram substance gave 0.5376 gram CO_2; and 0.1258 gram H_2O.

A portion of the acid was now carefully crystallised from pure alcohol, and then dried at the ordinary temperature. The results obtained with this specimen are:

XII. 0.2010 gram substance gave 0.4308 gram CO_2; and 0.1011 gram H_2O.

XIII. 0.1958 gram substance gave 0.4173 gram CO_2; and 0.0964 gram H_2O.

XIV. 0.1628 gram substance gave 0.3522 gram CO_2; and 0.0817 gram H_2O.

The results of the first six analyses do not agree well with each other, as will be seen in the following table in which the percentages of carbon and hydrogen are given:

	I.	II.	III.	IV.	V.	VI.
C	58.41	58.91	59.15	59.15	59.18	59.31
H	6.64	6.21	6.06	6.98	6.00	5.94

The variation in composition shown by these analyses we believe to be due to slight decomposition of the acid caused by boiling with water and alcohol.

The results of the remaining eight analyses agree fairly well with each other and also with those obtained by von Babo and Hirschbrunn, from which these writers concluded that the formula of the acid is $C_{11}H_{12}O_5$.

	Calculated for $C_{11}H_{12}O_5$.	Found.					
		VII.	VIII.	IX.	X.	XI.	XII.
C	58.93	59 08	58.58	58.76	58.65	58.76	58.45
H	5.36	5.83	5.11	5.72	5.56	5.60	5.59
				XIII.	XIV.	v. B. and H.	
				58.13	59.00	58.67	58.92
				5.47	5.58	4.87	5.67

The first six analyses led us to the suspicion that the composition might be $C_{11}H_{14}O_5$—with which formula the results of these analyses agree better than they do with the formula of von Babo and Hirschbrunn. In view of the results of the last eight, however, in which special precautions were taken to prevent decomposition, we think the evidence is overwhelming in favor of the original formula $C_{11}H_{12}O_5$.

Basicity of Sinapic Acid.

As above stated, von Babo and Hirschbrunn described and analysed a barium salt of sinapic acid, which was prepared by boiling the acid with an excess of baryta water. The composition of the salt as determined by them is represented by the formula $C_{11}H_{10}O_5Ba$, which requires 38.16 per cent. barium, while they found in two analyses 37.68 and 38.48 per cent. barium. This is the only salt analysed by them.

Our attempts to prepare crystallised salts were also unsuccessful. We nevertheless succeeded in analysing salts in solution, and in thus showing that the acid is really monobasic. For this purpose a weighed quantity of sinapic acid was brought into a flask with a small quantity of finely powdered Iceland spar, the mixture digested for some time on the water-bath, then boiled and filtered and the amount of calcium in the solution estimated.

0.2504 gram of the acid treated in the above manner gave 0.0329 gram CaO.

If the salt formed had been of the composition $C_{11}H_{10}O_5Ca$ the amount of calcium found would have been much greater, amounting to 15.27 per cent. of the total salt. The above weight of lime

corresponds, however, to only 8.65 per cent. calcium, assuming that the salt $(C_{11}H_{11}O_5)_2Ca$ has been formed; while this salt requires 8.23 per cent. calcium.

A similar result was obtained in an experiment with barium carbonate. 0.2005 gram of the acid was boiled with barium carbonate and water, filtered, and the amount of barium estimated by precipitating it as sulphate. The amount of sulphate found was 0.1144 gram. Assuming that the salt formed is $(C_{11}H_{11}O_5)_2Ba$, the sulphate found corresponds to 25.7 per cent. barium, while the salt requires 23.49 per cent. barium.

The salt described by von Babo and Hirschbrunn was also prepared and analysed by us. It was prepared directly from sinapine sulphocyanate by boiling with clear baryta water, care being taken to prevent access of air. It was then thoroughly washed with boiling water to remove all traces of baryta water. After drying it gave the following results:

I. 0.2035 gram dried at 130° gave 0.1285 gram $BaSO_4$.

II. 0.1998 gram dried at 140° gave 0.1266 gram $BaSO_4$.

	Calculated for. $(C_{11}H_{10}O_5)_2Ba$.	Found. I.	II.
Ba	38.16	37.13	37.25

Although our results do not agree with the calculated percentage as well as those obtained by von Babo and Hirschbrunn, they nevertheless point to the same conclusion. From all the above results taken together it follows that sinapic acid is a monobasic acid containing one hydroxyl, a conclusion expressed by the formula $C_{10}H_{10}O_2 \begin{cases} OH \\ COOH. \end{cases}$

Action of Acetyl Chloride and Acetic Anhydride on Sinapic Acid.

When sinapic acid is boiled with acetyl chloride it dissolves partly, and crystallises out unchanged. Even prolonged boiling produces no change in the composition. Acetic anhydride, however, easily dissolves the acid when boiled, and, if water is added and the solution allowed to cool, a white crystallised compound separates. This is easily soluble in hot water, from which it was crystallised. It fuses at 281°. The analyses gave the following results:

I. 0.2008 gram gave 0.4336 gram CO_2; and 0.1067 gram H_2O.

II. 0.2007 gram gave 0.4318 gram CO_2; and 0.1047 gram H_2O.

	Calculated for $C_{10}H_{10}O_2\{^{O.C_9H_9O}_{COOH}$	Found. I.	II.
C	58.65	58.89	58.68
H	5.26	5.91	5.80

This result confirms that obtained in working with the barium salts, and can leave little doubt that the acid contains one hydroxyl. It is clear from the above that sinapic acid is not a derivative of a hydroxy-phthalic acid.

Action of Potassium Hydroxide and other decomposing agents on Sinapic Acid.

When sinapic acid is thrown upon fused caustic potash it turns green and gives off vapors which have the odor of ordinary incense. The same odor is noticed very strikingly when a little of the acid is heated on platinum foil. If the acid is stirred with the fused alkali it gradually enters into combination, forming a dark brown colored mixture. Prolonged heating is necessary to cause the disappearance of lumps of unchanged acid. The fused mass was allowed to cool, dissolved in water and immediately acidified with hydrochloric acid. A black, gelatinous precipitate was thrown down. This was filtered off and found to be soluble in alkalies, forming a dark-colored solution, from which it was again precipitated on the addition of hydrochloric acid. The small quantity of the precipitate obtained prevented any further investigation of it. The filtrate from this precipitate was extracted with ether, and on evaporation of the extract there remained a small quantity of a substance soluble in water, the solution turning dark with alkalies. With ferric chloride and ferrous sulphate the aqueous solution gave a black or dark green color. In a second fusion with caustic potash the heating was not continued as long as in the first experiment nor was the temperature raised as high. From the ethereal extract of this fusion there was obtained a very small quantity of a substance which gave the reactions of pyrogallol. With ferric chloride it gave a red color. With ferrous sulphate a dark blue. With milk of lime it gave a reddish tint which soon changed to a brown. The solution reduced nitrate of silver. Although, in this as well as subsequent experiments, we were unable to isolate enough of the product to make a satisfactory determination of the fusing point, we believe that the reactions are sufficient to show that the

product of the fusion of sinapic acid with caustic potash is pyrogallol. A number of efforts were made to effect a satisfactory decomposition by means of caustic potash, but they were not more successful than the one described.

Taking the above facts into consideration, and recalling the properties of sinapic acid itself as established by von Babo and Hirschbrunn and confirmed by us, we can scarcely doubt that the acid is a derivative of gallic acid. The properties of the acid given by von Babo and Hirschbrunn more in detail than they have yet been stated, are as follows: The solution of the acid in caustic potash or soda changes very rapidly in the air. It passes through red to green and brown, and is transformed into other bodies. The ammonia salt turns reddish-brown. The precipitates with copper and lead salts are also rapidly changed, turning green or brown.

Thinking that possibly the decomposition of sinapic acid might be effected more perfectly by means of hydrochloric acid than by potassa, a small quantity was placed in a sealed tube with concentrated hydrochloric acid and then heated to 100° for 1½ to 2 hours. The sinapic acid entirely disappeared, the hydrochloric acid became dark red, and a dark-colored gelatinous precipitate was floating in the solution. This was filtered off and found to resemble closely the black gelatinous precipitate obtained from the fusion with caustic potassa. No other substance could be separated. The experiment was repeated with the same result.

Assuming that sinapic acid is in reality a derivative of gallic acid, an assumption which seems fully justified by the facts, there is but one view to be taken in regard to its nature. It must be

butylene-gallic acid, $C_6H_2\begin{cases} O \\ O \end{cases}>C_4H_8$, OH, CO_2H

At the beginning of our work we were for a time in doubt whether the composition of the acid is represented by the formula $C_{11}H_{12}O_5$ or $C_{11}H_{14}O_5$. Indeed the results of the first six analyses point rather to the latter formula as the correct one. We then further concluded that sinapic acid must be *diethyl-gallic acid*, $C_6H_2\begin{cases} OC_2H_5 \\ OC_2H_5 \\ OH \\ CO_2H \end{cases}$. We made a number of attempts to prepare this compound, but obtained nothing with exactly the properties of

sinapic acid. Finally we concluded to replace all the replaceable hydrogens of both sinapic and gallic acids with ethyl, hoping that thus we would in each case obtain the same final product, viz.: ethyl triethylgallate $C_6H_2\begin{cases}(OC_2H_5)_3\\CO_2C_2H_5\end{cases}$. In neither case, however, was a substance with characteristic properties obtained. The product was a dark-colored liquid which refused to solidify.

We propose to continue this investigation in the hope of effecting the synthesis of sinapic acid. The ethers of gallic acid can be made easily by starting from the lead compounds. For the purpose of comparison we shall attempt to make the methylene, ethylene, propylene and butylene ethers, and shall in due time communicate our results.

ON THE DETERMINATION OF NITROGEN BY COMBUSTION WITH CALCIUM HYDROXIDE.

(*From the Annual Report of the Connecticut Agricultural Experiment Station for* 1883, *communicated by* S. W. JOHNSON, *Director.*)

In a paper by the Director, published in the American Chemist for 1873 (vol. III, p. 161), it was shown that the mixture of sodium hydroxide and calcium hydroxide or oxide, proposed by Will and Varrentrapp as a reagent for converting organic nitrogen into ammonia for the purposes of analysis, may be advantageously replaced by a more easily prepared mixture of sodium carbonate and calcium hydroxide. When preparing that paper some combustions were made with simple calcium hydroxide; and in case of uric acid, for instance, the amount of nitrogen obtained fell short of the theoretical quantity by less than one per cent. As no entirely satisfactory results were then reached by burning with simple slaked lime, it was concluded that the presence of an alkali hydroxide, which it was thought might be formed in small quantity in the process of combustion, was necessary to the complete conversion of the nitrogen into ammonia. Further trials were then contemplated, but not until recently has the opportunity offered to carry them out. A series of analyses, whose results are here given,

demonstrate that this further simplification of the Will and Varrentrapp method applies to all those classes of substances which are ordinarily encountered in technical work.

The calcium hydroxide was prepared from a good quality of quicklime by slaking with water in but slight excess, drying off any surplus of water at a moderate heat, rubbing gently in a mortar, passing through a sieve of $\frac{1}{25}$ inch holes, and bottling in well-closed "fruit jars."

The tubes were filled and the combustions were made in the way indicated in the Report of the Connecticut Experiment Station for 1878, page 116. The points to be observed are chiefly these. For the burning of 0.5 gram of substances containing 8 per cent. of nitrogen or less, a tube of 14 inches is long enough. For dried blood or albuminoids containing from 12 to 17 per cent. of nitrogen a tube 2–4 inches longer is desirable.

The mixture of substance and slaked lime must not quite half fill the tube in lengthwise direction. The long anterior layer of slaked lime must be brought to a *full red heat* before heating the mixture, and must be so kept throughout the combustion.

No fumes or tarry matters, indicative of incomplete combustion, should appear in the bulb containing standard acid.

When the combustion proper is begun it may be carried on quite rapidly until completed.

The tube is cooled below a red heat before aspirating.

The ammonia from the combustion is received in standard hydrochloric acid and titrated with a standard ammonia solution, using tincture of cochineal as an indicator.

The advantages of using cochineal tincture instead of litmus solution are very considerable. It can be kept unaltered indefinitely, as litmus cannot; it is not seriously affected by the presence of carbonic acid in solutions, and as an indicator it is more sensitive.

In our use of the mixture of slaked lime and sodium carbonate, the acid in the bulb-tube is frequently colored more or less deeply red. This in nowise interferes with the alkalimetry, for the red color fades as the point of neutralisation is reached. In burning with simple slaked lime, the standard acid has almost invariably remained colorless, a fact which shows that the combustion with the latter is more perfect. It is evidently highly heated water vapor which at once oxidises the carbon and hydrogenises the nitrogen, and the slaked lime alone operates more effectually because it supplies more water in a given bulk of charge.

As was to be anticipated, the lime, at the full red heat to which it must be exposed, does not retain all the carbon dioxide that is formed; the gases which pass the standard acid give a copious precipitate in baryta-water. The standard acid, however, takes up from the heated gases too little carbon dioxide to sensibly affect the point of neutralisation, and the entire accuracy of the determination is in no degree impaired.

The contents of the tube, after the combustion is finished, are mostly quicklime with some carbonate, since they slake strongly and effervesce slightly in dilute acid.

The following are some of the results obtained by the two methods. Soda-lime here signifies the mixture of about equal bulks of sodium carbonate and slaked lime. The combustions have been executed by Mr. E. H. Farrington.

	Theory.	Soda-lime.	Slaked lime.
Crystallised potassium ferrocyanide,	19.93	19.82	19.86
Anhydrous " "	22.80	22.78	22.83
Potassium ferricyanide,	25.49	25.42 25.46	25.40 25.42
Strychnine,	8.38	...	8.30 8.32
Hippuric acid,	7.81	7.79	7.83
Dried oak leaves,	...	1.81	1.76
Dried chestnut leaves,	...	1.54	1.63
Wheat middlings,	...	2.28	2.30
Dried peat,	...	2.03	1.94
Castor pomace,	...	4.54	4.53
"Fish and Potash,"	...	2.48	2.39
" " " another sample,	...	3.75	3.75
Superphosphate,	...	3.46	3.37
Bone,	...	3.93	4.02
" another sample,	...	6.70	6.61
Fish scrap,	...	7.16	7.12
" " another sample,	...	7.61	7.70
Dried blood,	...	11.79 11.79	11.88 11.79
" " another sample,	...	11.18 11.23	11.26 11.33

In the case of bone, fish, and superphosphates, a still closer agreement would probably have been obtained by the two reagents if the materials analysed had admitted of finer pulverisation and more accurate sampling.

A considerably larger number of comparisons have been made, but in no case, except that of strychnine, was the difference greater than is indicated by the determinations above given.

The combustion of strychnine is more difficult than that of the other substances named above, and for good results it is needful to use it in small quantities, as seen from the subjoined statement.

			Soda-lime.	Slaked lime.
Strychnine	0.5 gram	tube 12–14 in.	7.82 7.85	7.89 7.98
"	0.3 "	" 14 "	7.44	...
		" 20–22 "	8.14 8.05	8.14 8.20
"	0.2 "	" 20 "	8.14[1]	8.25
"	0.1 "	" 20 "	...	8.30 8.32

REVIEWS AND REPORTS.

The Extraction of Sulphur.[2]

Sulphur is found either in superficial deposits, the result of volcanic emanations, constituting the *solfataras*, or else at a considerable depth underground, associated with calcareous and bituminous marls, gypsum, celestite, etc., forming the sulphur mines, which are the most important sources of this material.

The principal mines are in Sicily and in continental Italy.

The ore is gotten out with picks and is transported from the mine on the backs of men. Its extraction is effected by the partial combustion of the sulphur. This causes heat enough to fuse the remaining portion, which then flows into a hollow in the ground from which it is collected. In Sicily the sulphur is treated in a kiln, termed the *calcaroni*. It consists of a wall enclosing an inclined circular area, on which the ore is placed. The heap is covered with a layer of spent material thick enough to keep the combustion from proceeding too rapidly, and spaces are left here and there for the insertion of fagots of wood. The *calcarone* ready, the fagots are lighted, and the access of air so regulated as to avoid active combustion and too high a temperature. After the operation has been in progress a certain length of time, the operatives begin

[1] Will and Varrentrapp's Soda-lime, made by Merck.

[2] Translated from a paper by M. Camille Vincent in the Bulletin de la Société chimique.

collecting the sulphur and continue it until the ore is exhausted. In this operation considerable quantities of sulphur dioxide are produced, and in consequence of the difficulty of regulating the draught, much sulphur is wasted. Great damage is caused to the surrounding country, and any cultivation of the ground within a certain radius of the burning places is prevented. So great is this nuisance that the government of Italy forbids "burning the ore" between the first of July and the thirty-first of December.

The *calcaroni* yield but 50 per cent. (at most 60 per cent.) of the sulphur contained in the ore, the rest serving as the fuel, and thus producing torrents of sulphur dioxide. The imperfections of this process have for a long time given rise to numerous attempts to devise a more rational and less costly method of extracting the sulphur by the employment of some other kind of fuel. Heated air, steam under pressure, superheated steam, and carbon bisulphide to dissolve the sulphur, have in turn been proposed for the purpose of obtaining the greater part of the sulphur without the production of sulphurous acid fumes.

In the first of these methods, a chamber of masonry is filled with the ore, and a current of warm gas, from a hearth fed with wood or coal, is sent into it. This prevents in great measure the production of sulphurous acid, but the action is slow and the mass of ore is irregularly heated. A large amount of fuel is used and the number of hands is increased, so that the economy over the old method is very small.

The use of steam seemed at first sight to offer the best solution of the problem, for its action is very simple and rapid, and the sulphur obtained of good quality. The yield is better than in the *calcarone* process, and no sulphur dioxide is produced.

But the advantages of this method are counterbalanced in great part by the extra expense of purchasing and maintaining the equipment, as well as furnishing the fuel. The apparatus necessary are the boilers for heating the water, tanks to receive the ore, and other accessories. The water available for supplying the boilers is bad, rapidly forming crusts, which increase materially the cost of maintenance. Besides, the proportion of fuel used is considerable, in consequence of the large amount of steam necessary to heat the ore, as well as the loss of heat due to radiation from the uncovered surfaces of boilers, tanks, etc. This process cannot be applied in all cases, for the increased yield will not compensate for the greater cost of operating.

The treatment by carbon bisulphide, though very rational *a priori*, presents inconveniences that make its use impracticable. This solvent volatilises very rapidly, making it difficult and dangerous to work with, besides causing a considerable loss of material.

These difficulties have prevented the various processes from being used to any great extent, so that the old method of the *calcarone* is the one still generally employed.

In 1805 Thomas proposed immersing the ore in salt solutions heated to a suitable temperature. Balard, in 1867, thought the water from the salt marshes, which is rich in magnesium chloride, might answer. And finally, in 1868, Dépérais took out a patent in Italy for the extraction of sulphur by the immersion of its ores in a liquid heated 10° or 20° above its fusing point. By this means it is separated from the earthy materials associated with it. He used a solution of calcium chloride. The apparatus consisted of a spherical boiler of 2000 litres capacity, furnished with a stop-cock for drawing off the liquid sulphur, and surmounted by a vertical cylindrical part, into which, with the aid of a pulley, a basket of perforated iron, filled with the ore, can be let down upon a grate.

The apparatus is placed in a furnace and heated directly, while the cylindrical portion is surrounded by the warm gases passing up the chimney. The basket of ore is let down into the solution of chloride of calcium heated to 130°. The sulphur melts, collects in the bottom of the boiler, and is drawn off by the stop-cock and poured into moulds. When the ore is exhausted the basket is raised and immediately immersed in water contained in another boiler heated in the same furnace. This was used to supply the place of that lost by evaporation in the first.

At that time chloride of calcium was comparatively dear, so that the patent could not be worked successfully, and was soon abandoned.

Very recently this process has been taken up by MM. de la Tour and Dubreuil and put into practice by them with success.

Chloride of calcium is now very cheap, in consequence of the rapid development of the soda industry (the ammonia process). It can be put down at the sulphur mines in Sicily at 9 francs per 100 kilos.

The apparatus of MM. de la Tour and Dubreuil consists of two rectangular tanks, holding about 2 cubic metres each (2 m. × 1.30 m. × .75 m.). The bottom of the tanks is inclined $\frac{1}{10}$. They are placed in the same furnace and heated alternately by the same fire, which is fed with coke, lignite or coal. The ore is placed in one of these tanks, in which is also placed a solution of calcium chloride boiling at 120°. Heat is then applied, the sulphur melts gradually, and is drawn off directly into moulds by means of a spigot.

The whole operation lasts about two hours. The end is reached when the sulphur ceases to flow. The calcium chloride solution is then drawn off into the other tank previously charged with ore. Half of the liquid flows through a communicating tube, the rest is received in a vat built in the ground and is raised by a pump. The gangue is washed to regain the salt which it has absorbed, and this dilute solution is used in filling the tanks as occasion demands. The heat is then directed upon the second tank, and the first is cleared and recharged. There is no interruption in the

work, and the heat from the fire is all utilised. The sulphur obtained contains only .1 per cent. or .2 per cent. of impurity, whereas that obtained from the *calcaroni* contains from 2 per cent. to 3 per cent. There is left in the gangue but 4 per cent. or 5 per cent. of the sulphur originally contained in the fresh ore.

In this treatment certain ores are completely disintegrated, in consequence of the fusion of the sulphur, which is then mixed with earthy matter. MM. de la Tour and Dubreuil in order to overcome this great inconvenience were compelled to change completely the plan of their apparatus. The new plan which they adopted is applicable to the treatment of ores of all kinds.

The tanks are built horizontal, and are divided longitudinally through the centre by a gutter with inclined sides, which collects the sulphur, and from which it is drawn. On its two sides iron gratings are built vertically to keep the ore from falling into it. These gratings are made of bars of sheet iron 2 mm. thick and 25 mm. wide, placed 3 mm. apart. By this new arrangement they can treat ores of all kinds, even the fine powder formed in mining the ore. This powder is very rich, and is known in Sicily as *sterri*. It was formerly left at the mines. This *sterri* is always richer than the average of the mined ore, for in getting the ore out, the rock breaks and divides along the lines of least resistance, which in this case are the veins of sulphur. On account of its friability the sulphur is reduced partially to dust and forms a large part of the mixture.

At the Tronica mine, in the province of Caltanisetta, in Sicily, the ordinary ore gives 21 per cent. of sulphur when treated by the calcium chloride method, while the *sterro* yields 72 per cent. The average yield of the Sicily ore, treated in the *calcarone*, is from 12 per cent. to 13 per cent. In some few cases it reaches 17 per cent.

On comparative treatment the same ores yielded from 10 per cent. to 12 per cent. by the *calcarone* process, and from 19 per cent. to 23 per cent. by fusion in chloride of calcium bath.

It has been known for a long time that ores very rich in sulphur acted badly in the *calcarone*. The combustion is too rapid, and the sulphur, browned and viscous from overheating, is hard to draw off. In order to treat such ores it is necessary to mix them first with inert material when the yield is not in accordance with the primitive richness of the ore. These rich ores are, on the contrary, treated advantageously in the chloride of calcium bath.

After the treatment of a large amount of *sterri*, MM. de la Tour and Dubreuil estimated the cost of extraction of a ton of sulphur at 12 fr. 75c. in the case of a mean yield of 33 per cent. of the weight of the ore.

The cost of treatment of one charge (about 1000 kilos) in their apparatus, is as follows:

35 kilos. fuel (coal mixed with lignite) @ 30 fr. per ton,	1 fr. 5c.
14 " chloride of calcium, 2 per cent. carried away by gangue after washing, @ 9 fr. for 100 kilos.,	1 25
Labor,	1 25
Unforeseen, general expenses, 20 per cent.,	70
Total,	4 fr. 25c.

Thus, in order to obtain a ton of sulphur, three charges must be worked, making the cost of extraction 12 fr. 75c. per ton.

An operation with *sterri* requires an hour and a quarter for fusion, a quarter of an hour for drawing the sulphur, and an hour and a half for washing the gangue and letting it drain, clearing the tank and putting the movable gratings back in place.

MM. de la Tour and Dubreuil have already introduced a number of their tanks in the sulphur region, principally for working up the *sterri*. There are three at the Tronica mine, in the province of Caltanisetta; two at the Grottarossa mine, in the same province; two at Pernice, near Recalmuto, and two at the mine Crocca.

The method just considered presents great advantages over the older methods:

1st. It allows the extraction of the greater part of the sulphur from ores of every kind, at a minimum cost for fuel.

2d. The extraction is effected regularly, protected from atmospheric influences.

3d. Work is carried on throughout the year, as no sulphurous acid fumes are formed.

4th. It permits the treatment of the ores according to the demands of the trade.

W. S. B.

STARCH AND ITS TRANSFORMATIONS UNDER THE INFLUENCE OF ACIDS.

The views concerning the transformation of starch into sugar by boiling with sulphuric acid, or the action of diastase, have been so contradictory that the nature of the changes which starch undergoes in this transformation has remained entirely open to question. Quite recently, however, F. SALOMON[1] has succeeded by a very elaborate investigation in placing the reaction on a satisfactory basis.

Musculus was of the opinion that by the action of diastase, as well as sulphuric acid, starch is split up into two molecules of dextrin and one molecule of sugar; and later the acid acts on the dextrin thus formed, though very slowly. The first decided contradiction to this view was furnished by Payen, who asserted that starch did not split up in the manner described by Musculus, either under the influence of diastase or sulphuric acid, but rather that there was a gradual transformation. The fact that these two opposed

[1] Journal für practische Chemie, **28**, 65.

views have been advocated by various subsequent investigators serves to show that considerable difficulty is involved in the settlement of the question. The announcement by Soxhlet of the inexactness of Fehling's sugar test showed that the key to this difficulty must be sought in improved methods for the determination of the substances which appear in the process. Salomon has, therefore, first studied the beginning and end products of the reaction, *i. e.* starch and dextrose, and also the intermediate products, "soluble starch," dextrin and maltose, particularly with regard to the analytical processes involved in their determination.

Starch.

The methods given in the text-books for the quantitative estimation of starch are based usually upon the conversion of starch into dextrose (glucose, starch sugar) with the aid of dilute sulphuric acid, and the subsequent determination of the sugar by reducing solution of copper. But Allihn has shown that starch is never entirely converted into sugar by this means, and that 95 per cent. is the maximum that can be converted into sugar by sulphuric acid under the most favorable circumstances. But if hydrochloric acid is used according to the method of Sachsse, a complete conversion may be effected. This method of Sachsse yields satisfactory results as regards the conversion of starch into sugar, but Salomon differs from Sachsse in the formula obtained by it for starch, *i. e.* $C_{36}H_{62}O_{31}$, containing one molecule of water more than required for a hexapolymer of $C_6H_{10}O_5$. Salomon has found by the specific gravity and specific rotatory power of the converted starch, and also by gravimetric determinations of the sugar by Allihn's method, that from 100 parts starch 111.1 parts of dextrose are obtained, a result which agrees very closely with the theoretical, supposing the reaction to be

$$\underset{\text{Starch.}}{C_6H_{10}O_5} + H_2O = \underset{\text{Dextrose.}}{C_6H_{12}O_6}$$

The deviation from the proportion observed by Sachsse was probably due to insufficient drying of the specimens of starch used in the analyses.

The determination of the amount of moisture in starch is by no means as simple as might appear from casual observation. The author has found that if starch is dried at any given temperature between 100° and 130°, the loss of moisture is nearly constant for this temperature for the same variety of starch. As soon as the temperature rises above 120°, even at 125°, all the kinds of starch begin to turn yellow, and therefore a deeper decomposition undoubtedly begins at this point. But the loss of water is most constant at 120°. From the fact that starch dried at this temperature yields more sugar than that dried either below or above, the complete drying can be effected only at this temperature. It must be

allowed to cool in a sulphuric acid desiccator, as it will take moisture from calcium chloride. After the conversion of starch into sugar by the aid of hydrochloric acid, the sugar is determined by the gravimetric method of Allihn with the precautions observed by Soxhlet. If pure sugar solutions are used the results are identical with those given by Allihn, but if, on the contrary, the solutions contain other substances, good results can only be obtained when care is taken that nearly all the copper solution used is reduced. Good results may be obtained even in dilute solutions when the sugar is made from potato or rice starch, but with corn starch certain irregularities in the reduction can only be explained by supposing the presence of a reducing substance in corn starch or formed during its conversion into sugar. The numbers obtained with dilute solutions were too high, and only approached the theoretical amount when one per cent. solutions were used, so that an "after reduction," as it is called by Allihn, could not take place.

Dextrose.

The author makes use of the following facts in studying the transformation of starch into this substance:

1. Dextrose dissolves easily in water and dilute alcohol.
2. An aqueous solution of iodine effects no perceptible change in the sugar solutions.
3. The specific gravity of a solution containing 10 grams of dried dextrose in 100 cc. water is 1.0381.
4. The reducing power of dextrose may be conveniently estimated by Allihn's method.
5. The specific rotatory power of dextrose is: $\alpha j = 58.68°$.

A similar study of maltose shows: 1. Solubility in water and strong alcohol. 2. Indifference towards iodine. 3. 10 grams of dry maltose in 100 cc. water at 17.5° give a specific gravity 1.0390. 4. 1 gram dry maltose in 100 cc. water rotates the plane of polarisation 8° in a 200 mm. tube of the Jellet-Cornu apparatus. 5.1 gram dry maltose corresponds to 1.13 grams of copper.

Soluble Starch.

This substance was first obtained by Jaquelin in 1840 by heating starch paste to 150°. Its importance in the present investigation lies in the fact that it is also formed by the action of dilute sulphuric acid on starch. It is a white, soft, bulky powder, insoluble in cold water, but easily soluble at 80–100 degrees, forming a clear, transparent liquid that has none of the pasty character of solutions of ordinary starch. The pure substance gives a deep blue color with iodine, but if care is not taken to separate dextrin the color is a red-violet. It does not affect Fehling's solution under the ordinary conditions of Allihn's method of sugar estimation. An aqueous 1 per cent. solution has a specific gravity of 1.0041. It rotates the plane of polarisation +11.91° in a 200 mm. tube of the Jellet-Cornu apparatus.

Dextrin.

The literature concerning dextrin contains many statements greatly at variance in regard to the properties of this substance. These inconsistencies seem to be due to the great difficulty of obtaining pure dextrin free from sugar or maltose, and also to the difference in the reaction with iodine which these impure specimens display. Pure dextrin may be obtained by the action of sulphuric acid on starch if care is taken to stop the process early enough. The solution thus obtained gives no reaction with Fehling's solution under the conditions of Allihn's method. By continued purification dextrin can be obtained which gives only a very slight brown-red color with aqueous iodine solution, and this color is so out of proportion to the amount of dextrin used as to satisfy the author that it is due to a slight admixture of sugar and that pure dextrin gives no color with iodine. Dextrin is precipitated from its aqueous solutions on the addition of alcohol. Its specific gravity in 10 per cent. solution is 1.038. The specific rotation in neutral aqueous solution is $aj = 216.5°$, or 1 gram dissolved in 100 cc. water gives 11.3° in a Jellet-Cornu apparatus. This specific rotation appears to be greater in acid than in neutral solutions.

Examination of the Process of Starch Transformation.

With analytical data, the action of dilute sulphuric acid was studied in the following way: An apparatus was arranged in which a certain amount of starch solution could be boiled at a fixed concentration, and from which portions could be easily taken for analysis at regular intervals. These portions were examined as to their action on iodine solution, their rotatory power and specific gravity. As many as sixteen observations were recorded in one of these boiling processes which were sometimes continued for twenty-eight hours. By a study of the iodine reaction, and observing how the time of boiling and the concentration of the acid affect the reaction of iodine solution on the transformation products of starch, it is seen: 1. That the change from one color to another is very gradual. 2. That it always takes place in exactly the same order, *i. e.* from deep blue to violet, red-violet, red, red-brown, brown-yellow, yellow, and finally colorless. 3. That neither the complete extinction of the color nor the individual shades correspond exactly with the amount of sugar formed as shown by the rotatory power. The color changes may be ascribed to the soluble starch alone, and the color which this substance gives with iodine depends upon the concentration, the temperature, the amount of dextrin, and the degree of subdivision of the latter substance.

From considerations of the changes in rotatory power and the action of Fehling's solution it is seen that the conversion of starch proceeds more rapidly in proportion as the acid is stronger; by doubling the amount of acid the conversion is nearly twice as

rapid. The conversion is very gradual, proportional to the time, and becomes somewhat slower as the end of the process is approached. It proceeds in inverse proportion to the observed rotation, which changes nearly inversely as the reducing power until all the dextrin is converted into sugar, and longer boiling still decreases the rotatory power slightly. The end point is reached at 34.0° of the Soleil-Ventzke-Scheibler apparatus.

Another series of experiments shows that after boiling starch with sulphuric acid 2¾ hours, the solution contains soluble starch, dextrin, dextrose, and perhaps maltose.

By boiling for another hour the soluble starch disappears, and the examination of the specific gravity, reducing action and optical conduct, show that maltose is probably absent, and give data for calculating the proportion of dextrose and sugar. After the second boiling the quantities of sugar and dextrin are about equal. At the end of the fourth hour there is about twice as much sugar as dextrin, and then the proportion changes at a slower rate, until at the end of the seventh hour there is about seven times as much sugar as dextrin, but further than this the examination could not be carried with satisfactory quantitative results.

By studying the action of other acids on starch the author finds that organic acids are also able to effect the transformation into sugar. Oxalic acid particularly when used in equal amount with the sugar converts it entirely into sugar in three hours; a fact which is used largely in the actual manufacture of starch sugar.

Citric and tartaric acids require a much longer time than sulphuric acid for the transformation of starch even when used in much larger quantities, but they furnish chemically pure dextrose.

According to the experience gained in the course of the work, the action of sulphuric acid consists in transforming the starch molecule, which probably consists of a union of several groups $C_6H_{10}O_5$, into the simpler soluble starch, and this into dextrin. This phase of the process is accomplished with remarkable rapidity, so that the second phase, the hydration of the dextrin into sugar, begins almost at the same time.

Since the formation of sugar is intimately connected both with the time and also with the concentration of the acid, so that a double amount of acid converts twice as much starch into sugar in a unit of time, the process may be represented as very similar to the formation of ether.

Sulphuric acid unites with a certain amount of the dextrin, hydrates it, and gives it up again to unite with a new quantity of dextrin and convert it in turn into sugar.

D. T. D.

NOTES.

Historical Note concerning the Presence of Carbon in Phosphorus.

In connection with the observations of Mr. Keiser and myself which prove the presence of carbon in ordinary phosphorus, it is interesting to note the fact that this subject was actively discussed in the early part of the present century. The discussion was started by Proust[1] in 1799, who described a compound which he called phosphide of carbon (phosphure de charbon), obtained as a residue in purifying phosphorus. According to Proust, when the phosphide is treated with nitric acid a mixture of carbonic acid and the oxides of nitrogen is given off.

Later Steinacher[2] confirmed the observation of Proust, and stated that it was impossible to completely remove the carbon from phosphorus. The evidence which he put forward is, however, not convincing.

In 1812 Thenard[3] stated in the most positive way that the purest phosphorus that could be made contained carbon; and that when phosphorus is burnt slowly in the air, not only phosphorous acid, but also carbonic acid is formed; though he adds that when phosphorus is burnt rapidly no carbonic acid is obtained.

In 1813 Vogel[4] denied the presence of carbon in phosphorus, his opinion being based mainly on the fact that, according to him, no carbonic acid is formed when phosphorus is treated with nitric acid.

In 1816 Thomson[5] described phosphide of carbon obtained from phosphorus, and even gave the results of an analysis which showed that the compound contained 38 per cent. carbon and 62 per cent. phosphorus.

Finally, in 1818, Davy[6] stated that by treating phosphorus with chlorine he had convinced himself that it contained no carbon. Since that time the matter appears to have been dropped. Evidently this statement coming from Davy, who at that time was at the height of his renown, carried conviction with it.

It is difficult to see how the absence of carbon could be positively proved by Davy's method. Apparently Davy held that the chlorine would unite with the phosphorus and leave the carbon as such behind. But, if the carbon were in combination with the phosphorus, it might, and probably would, unite with chlorine,

[1] Scherer's Journal der Chemie, **7**, 234 (1801).
[2] Gehlen's Journal der Chemie, **1**, 679 (1803).
[3] Annales de Chimie, 1812, 109; abstract in Schweigger's Journal für Chemie und Physik, **4**, 212.
[4] *Ibid.* **7**, 109.
[5] Schweigger's Journal für Chemie u. Physik, **18**, 368.
[6] Philosophical Transactions, 1818, Part 2.

forming a compound which when mixed with the chlorides of phosphorus it would be difficult to detect.

It appears then that the only experiment in which all possible sources of error have been avoided is that of Mr. Keiser and myself, and though this experiment opens anew an old question, it at the same time furnishes a final answer.

I. R.

On the alleged Transformation of Brucine into Strychnine.

Sonnenschein[1] announced in 1875 that when brucine is gently heated with dilute nitric acid, carbonic acid gas escapes, while the solution contains a yellowish resin and strychnine, which may be extracted by saturating with potash and treating with ether. On the other hand, according to Laurent and Gerhardt and to Hofmann, there is formed in this reaction methyl nitrate and a nitrogenous base, cacotheline. The identity of the resin obtained by Sonnenschein with this latter is evident, and M. Hanriot has endeavored to verify the existence of strychnine among the products of the reaction. In operating, however, in precisely the same manner described by Sonnenschein, but with purified brucine, he has not been able to discover the slightest trace of strychnine, the qualitative reaction of which is, as is well known, extremely delicate. He therefore concludes that the strychnine found by Sonnenschein pre-existed in his incompletely purified brucine.

M. HANRIOT has further discovered that when brucine contains even as large a quantity as half its weight of strychnine the latter cannot be discovered by its ordinary reaction, so that it does not suffice to try a specimen of brucine by the reaction with sulphuric acid and potassium bichromate to conclude that it is free from strychnine.

If a mixture of brucine (2 parts) and of strychnine (1 part) be heated in the manner described by Sonnenschein, the strychnine can readily be discovered by its reaction after the brucine has been destroyed by the nitric acid; or more simply, if a mixture of the two bases in sulphuric acid, containing a drop of nitric acid, be allowed to stand in a watch-glass, strychnine can be discovered after two hours. A large number of substances are thus capable of masking the reaction of strychnine, among them morphine, quinine, and methyl alcohol, though this has a more feeble action.

It will be seen that the recognition of strychnine in brucine presents a certain amount of difficulty, and inasmuch as physiological properties have been attributed to brucine which resemble those of diluted strychnine, it becomes of interest to inquire whether the specimens of brucine operated with up to this time have really been free from strychnine. M. Hanriot is at present investigating the purification of brucine.—(*Comptes Rendus*, **97**, 267.)

R. D. C.

[1] Berichte der deutschen chemischen Gesellschaft, **8**, 212.

A Simple Method of Extracting Caesium and Rubidium Compounds from Hebron Lepidolite.

Lepidolite from Hebron, Maine, has been shown to contain caesium and rubidium in considerable quantities. The following is a simple and effective method of obtaining the compounds of these metals.

The mineral is pounded in an iron mortar until it feels soft to the touch; mixed in the mortar with an equal weight of fluor-spar, and the two ground together for a few minutes to secure intimate mixture. The mixture is transferred to a leaden dish, made into a thin paste with common strong sulphuric acid, and heated on a sand bath for two or three hours or until the mass is hard and dry.

When cold the mass is broken up, placed in a porcelain dish, and boiled out three times with water, the water in each case being poured, while hot, through a filter.

The filtrate contains caesium, rubidium and potassium as alums. These alums are about equally soluble in hot water, but at 17° the potash alum is nearly six times more soluble than the rubidium alum, and twenty-two times more soluble than the caesium compound (Redtenbacher). Hence it is easy, by means of these differences, to separate the rubidium and caesium compounds from the last traces of potassium, and from each other.

1000 grains of lepidolite, treated in the above manner, yield about 30 grains of caesium and rubidium alums.

The process seems to commend itself on account of: (1) Its cheapness—the only reagents used being common fluor-spar and sulphuric acid; (2) the short time required—but a single day; (3) avoiding the use of platinic chloride, and fusion of the mineral.

F. C. ROBINSON and C. C. HUTCHINS.

BOWDOIN COLLEGE, *July* 2, 1883.

The Production of Metallic Titanium by the Action of Sodium at Low Temperatures.

An experiment was made with a view towards forming titanium trichloride, Ti_2Cl_6, by the action of sodium upon the tetrachloride, $TiCl_4$.

A small ignition tube was one-third filled with the anhydrous tetrachloride, and sodium in small pieces dropped in, in quantity sufficient to fill the tube nearly to the level of the liquid. The tube, after being sealed, was exposed to the action of a steam bath for 10 hours. At the end of this time the pieces of sodium were found to have a black coating of metallic titanium.

When heated to 130° the action became more rapid, the pieces of sodium still retaining their shape, but becoming somewhat honeycombed. At 150° a violent reaction took place, breaking the tube. The lumps remained of the same general form and dimensions as the lump of sodium used, but, after the experiment, they contained only a small central bit of sodium, the remainder being a thick crust of titanium.

Further experiments will be made with a view towards ascertaining the lowest temperature at which the metal can be produced.

F. C. ROBINSON and C. C. HUTCHINS.

BOWDOIN COLLEGE, *July* 2, 1883.

Concerning the Thiophene and Pyrrol Groups.

VICTOR MEYER continues his studies of the substances related to thiophene recently found by him in ordinary coal-tar benzene. He again calls attention to the remarkable resemblance of the derivatives of thiophene to the corresponding ones of benzene. As monobrom-thiophene can be obtained only with difficulty he has been unable to make methyl-thiophene by Fittig's method. On the other hand, it is probable that in coal-tar xylene as well as toluene the homologues of thiophene are contained. That contained in toluene has been separated, though not in pure condition, and it has been shown to be methyl-thiophene, as was anticipated. To obtain this substance the sulphuric acid extracts of about two tons of toluene were worked up. By distilling the lead salt of the sulphonic acid with ammonium chloride, several kilograms of an oil were formed, which after a few distillations boiled at 110°. This was found to consist of about 15 per cent. of methyl-thiophene and 85 per cent. of toluene. Although it was found to be impossible to isolate the methyl-thiophene in pure condition, its dibrom-substitution product, $C_4HS\begin{cases}CH_3\\Br_2\end{cases}$, was obtained without difficulty.

Thiophene is the mother-substance of a large number of beautiful coloring matters. In general, it was shown that ketones, which contain only carbon, oxygen and hydrogen, give colored products, if they contain the group CO–CO. Simple ketones or those double ketones which do not contain the two carbonyl groups in direct combination do not give colored products. Colored products have been obtained from: phenyl glyoxylic acid and thiophene (violet red); benzil and thiophene (blue); phenanthrene-quinone and thiophene (green); phenanthrene-quinone and methyl-thiophene (violet); alloxan and thiophene (deep blue).

Meyer has also shown that pyrrol, C_4H_5N, acts towards the ketones very much in the same way that thiophene does, especially in the matter of yielding colored products. This fact points to an analogy between the structures of the two substances. If thiophene be regarded as benzene in which two CH groups are replaced by a sulphur atom, as represented in the formula, $\begin{matrix}CH=CH\\|\\CH=CH\end{matrix}>S$, pyrrol may be regarded as benzene in which two CH groups are replaced by NH as represented thus, $\begin{matrix}CH=CH\\|\\CH=CH\end{matrix}>NH$. — (*Berichte der deutschen chemischen Gesellschaft*, **16**, 2968.)

The Liebig Monument.

Last November the beautiful monument of Liebig which had been unveiled in Munich only a few months previously, was found to have been horribly disfigured by a large number of stains, about three hundred in number, which apparently had been applied by some human fiend standing upon the marble pedestal. The city government called in Professors von Pettenkoffer and Baeyer and Dr. C. Zimmermann, all of the University, to determine the nature of the stains and, if possible, to remove them. They soon found that the principal substance which had been used was nitrate of silver with which permanganate of potassium had been mixed. The stains had worked their way into the marble several millimeters.

The committee experimented in a number of ways upon pieces of marble stained with the substances believed to have been used, and succeeded in devising a method for completely removing the stains without injury of any kind to the marble. The method consists in first converting the metals, silver and manganese, into the sulphides and then dissolving these in a solution of potassium cyanide. In order to apply the reagents to the statue, they were mixed with finely powdered porcelain clay so as to form a paste. A paste saturated with ammonium sulphide was first applied to all the spots and allowed to remain for twenty-four hours. It was then removed and replaced by a fresh paste containing the same reagent, which also was allowed to remain for a day. After removing this paste the spots were washed with water, and a paste containing a concentrated solution of potassium cyanide applied. This was once removed and renewed, and the spots then found to have disappeared entirely. The statue is now again in perfect condition, subsequent exposure to the sunlight having produced no effect upon the cleansed parts.—(*Berichte der deutschen chemischen Gesellschaft*, **17**, 230.)

At the last annual meeting of the German Chemical Society, Professor Wolcott Gibbs, of Harvard University, was elected an honorary member of the society. Professor Gibbs is the first American upon whom this honor has been conferred. Its significance will be appreciated when it is stated that the list of honorary members is a very short one and includes such names as Bunsen, Kopp, Berthelot and Frankland.

A few friends of Professor A. W. Hofmann have had a gold medal prepared to be presented to him in commemoration of his visit to this country. Upon one side is a very good bas-relief profile of Hofmann, and upon the other the simple inscription: "To A. W. Hofmann: from his friends and admirers in the United States of America, October, 1883." Bronze copies of the medal have been prepared for the subscribers to the fund.